QUALITATIVE ANALYSIS

WORKS TRANSLATED BY WILLIAM T. HALL

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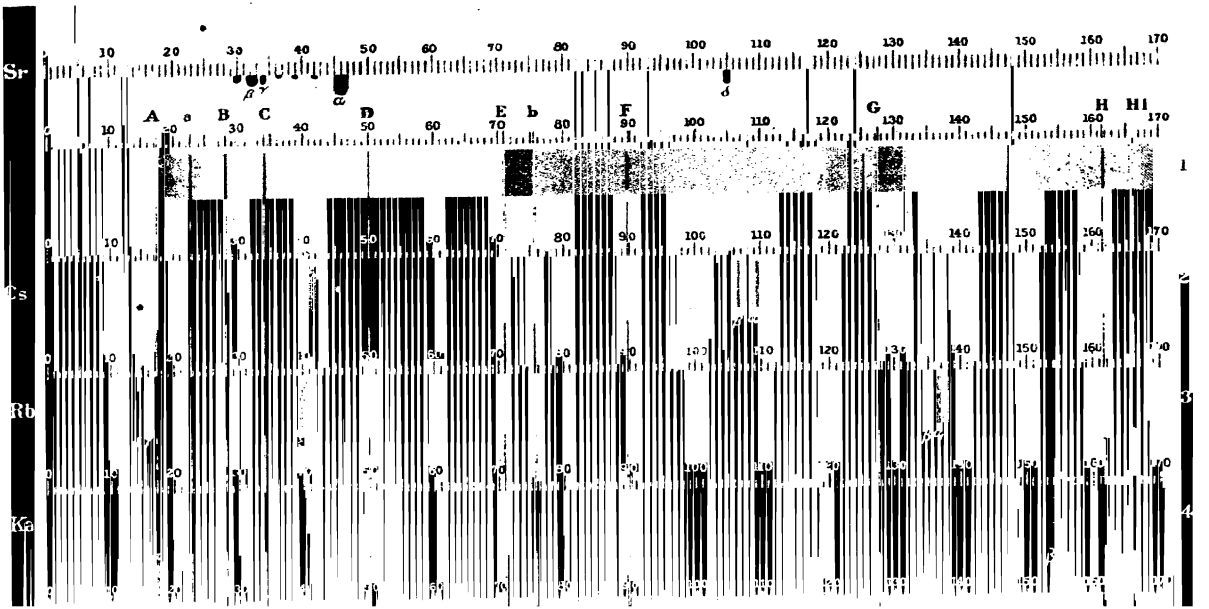
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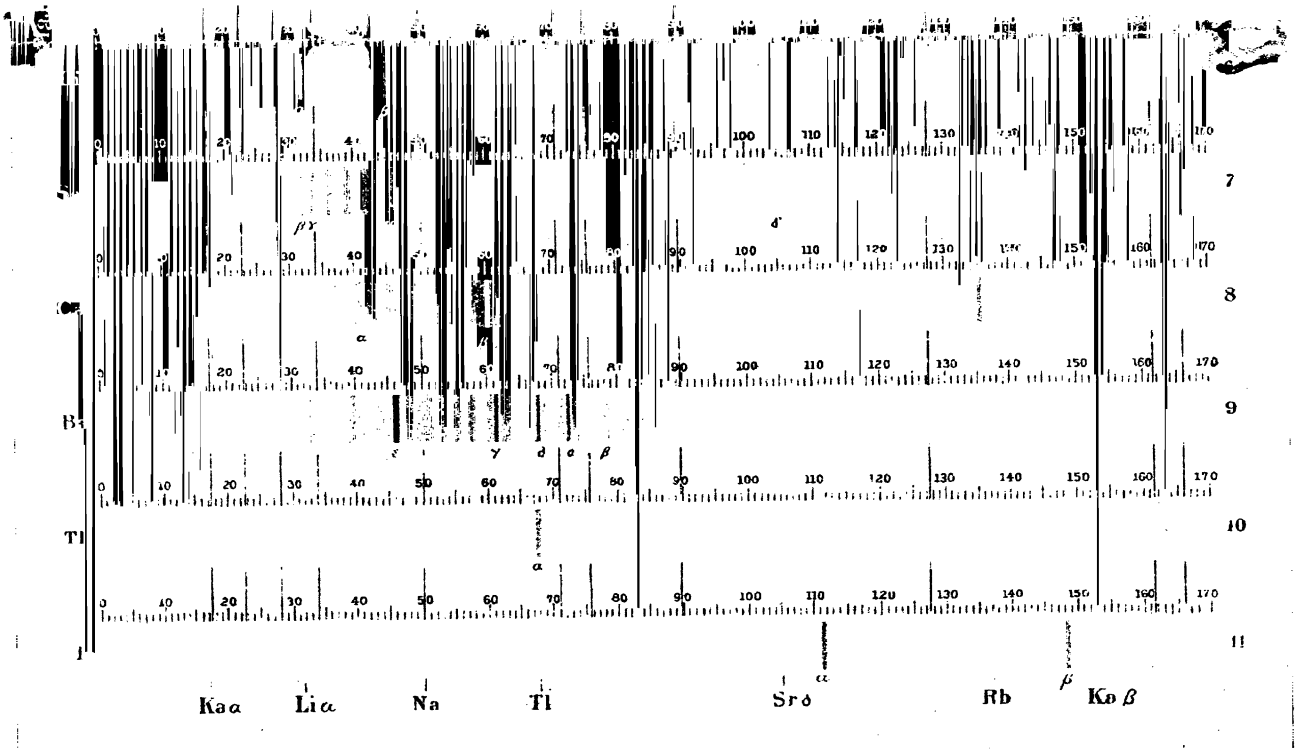
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Analytical Chemistry

BASED ON THE GERMAN TEXT

OF

F. P. TREADWELL,

Late Professor of Analytical Chemistry at the Polytechnic Institute of Zurich

TRANSLATED AND REVISED

BY

WILLIAM T. HALL, S.B.,

Associate Professor of Analytical Chemistry, Massachusetts Institute of Technology

VOLUME I

QUALITATIVE ANALYSIS

FIFTH ENGLISH EDITION

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PREFACE TO THE FOURTH ENGLISH EDITION

The German text upon which this book is based was written by an American who taught for many years at Zurich. The first English edition appeared as an authorized translation by one who had been teaching analytical chemistry for only three years at that time. It was translated largely as a result of a chance remark of his assistant, R. W. Balcom, who deplored the fact that the students could not read German readily enough to make use of the German text as a reference book. At that time, the translator was using, as he has always used, the excellent book of A. A. Noyes as a laboratory manual in Qualitative Analysis and the extremely useful text of H. P. Talbot for the preliminary work in Quantitative Analysis. The results obtained by asking the students to purchase both volumes of this book in addition have been exceedingly gratifying. Better examination papers have resulted and there have been fewer unnecessary questions asked in the laboratory.

Recently Professor Noyes has greatly changed his text on Qualitative Analysis and this has unquestionably had considerable influence upon the preparation of the fourth English edition of this book. It has been so thoroughly revised and so largely rewritten that it is no longer fair to Professor Treadwell to publish the book as a literal translation, although the writer remains in thorough sympathy with Professor Treadwell's views and does not wish, in any way, to disclaim the great benefit and inspiration he has derived from close study of the original text. He must, however, express his obligation to other texts, particularly to those of Noyes, Stieglitz, Böttger, and Ostwald, from which many of the ideas introduced into this text have been borrowed. The general plan of the book has been kept the same, but greater stress has been laid upon the theoretical side of the subject, particularly with regard to the applications of the mass action principle, the ionization theory, and the theory of oxidation and reduction.

The translator wishes to acknowledge his indebtedness to Mr. Donald Belcher, who has read all the proofs of this edition and offered many valuable suggestions.

WILLIAM T. HALL.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
February, 1916.

PREFACE TO THE FIRST EDITION

Having been repeatedly requested by former pupils to publish the lectures on Analytical Chemistry given by me at this Institute since 1882, and not having time then to do it myself, I permitted the "Verein der Polytechniker" in 1885 to print in manuscript form the notes of one of my students.

This output met with such a friendly reception that in 1888 a second edition became necessary. Subsequently I decided to revise the material thoroughly and publish it in book form; this text-book of Analytical Chemistry represents, therefore, a somewhat amplified repetition of my lectures.

The book is intended not only for laboratory use, but also for self-study. With each element the mineralogical occurrence, crystalline form, and isomorphous relations are briefly mentioned. Then, after explaining the reactions, the methods of separation are given in the form of tables; because, contrary to the views of many, I have in this way obtained the best results in teaching. These tables are summarized charts by which the student can quickly find his bearings.

Much weight is placed upon the determination of the sensitiveness of the single reactions, as explained on page 78, because in this way the beginner becomes at once familiar with the solubility of the most important salts, and also with simple stoichiometrical calculations. The approximate solubility of potassium chloroplatinate, for example, is found from the following determination of the sensitiveness of the reaction by which it is formed:

If 100 cc. of the solution contain 0.156 gm. potassium, one finds that the formation of the chloroplatinate, at ordinary temperatures, takes place only on addition of a little alcohol; but on increasing slightly the amount of potassium in the solution, it takes place immediately. We can, therefore, assume that the solution, which contains 0.156 gm. of potassium per 100 cc. water, is saturated with chloroplatinate; hence the amount of the latter may be calculated:

$$K_2 : K_2PtCl_6 = 0.156 : x;$$
$$78.3 : 485.8 = 0.156 : x;$$
$$x = 0.97.$$

The result shows that 100 cc. of water, at ordinary temperatures, dissolve 0.97 gm. of K_2PtCl_6, while accurate determinations at 20° C. have given the value 1.12. The difference, about 12 per cent, is explained by the facts that we did not work at exactly 20° C., nor with absolutely pure water; the solution also contains an excess of chloroplatinic acid, whereby the solubility of the potassium chloroplatinate is diminished; evidently the values obtained in this way permit a very good comparison of the solubilities of the different salts. From the sensitiveness of the reaction between a potassium salt and tartaric acid, the solubility of the potassium acid tartrate may be found to be 0.38; so that the solubility of the potassium chloroplatinate is to that of the potassium acid tartrate as 0.97 : 0.38; the potassium tartrate is about three times as insoluble as the chloroplatinate, etc.

The size of the book does not permit going into the microchemical detection of the different elements. We have, however, in the excellent work of H. Behrens, "Anleitung zur mikrochemischen Analyse," a reference book of the highest rank.

In publishing this, the first volume of the work, I beg of my colleagues and fellow chemists to kindly inform me of any errors or omissions.

F. P. TREADWELL.

ZURICH, April 29, 1899.

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Qualitative Analysis

PART I. GENERAL PRINCIPLES

Analytical Chemistry covers all those operations which are performed in order to determine the constituents of a chemical compound (or a mixture of chemical compounds). Analytical Chemistry is subdivided into Qualitative Analysis and Quantitative Analysis.

Qualitative Analysis treats of the methods for determining the nature of the constituents of a substance. Quantitative Analysis treats of the methods for determining *in what proportion* the constituents are present in any compound or mixture of compounds.

In order to recognize a substance we change it, usually with the help of another substance of known nature, into a new compound which possesses distinctive properties. This transformation we call a *chemical reaction;* and the substance by means of which the reaction is brought about, the *reagent.*

We distinguish between reactions in the *wet way* and reactions in the *dry way.*

I. Reactions in the Wet Way

For the purpose of qualitative analysis only such reactions are applicable as are easily perceptible to our senses. A reaction is known to take place — (*a*) by the formation of a precipitate; (*b*) by a change of color; (*c*) by the evolution of a gas. In other words, the sense of sight is used chiefly in qualitative analysis and most of the reactions employed are visual ones. The sense of smell also aids in identifying many substances. Thus the vapors of hydrogen sulfide, hydrogen cyanide, bromine, carbon disulfide and a great many other substances have very characteristic odors. Some of these vapors are poisonous, so that in trying the odor it is best to waft a little of the vapor, by a motion of the hand over the substance to be tested, in such a way that the vapor reaches the nostrils greatly diluted with air. The sense of taste is sometimes useful, but is rarely employed on account of the danger of poisonous effects. The sense

of touch sometimes furnishes a little aid; thus graphite has a peculiar, greasy feeling, and paralysis of the tongue or eyelid is temporarily imparted by the alkaloid cocaine and certain allied substances.

When an aqueous solution of barium chloride is mixed with dilute sulfuric acid, a white crystalline precipitate of barium sulfate forms:

$$BaCl_2 + H_2SO_4 = 2HCl + \mathbf{BaSO_4}.$$

A precipitate of identically the same chemical composition can be formed from any other soluble barium salt or by using a solution of any soluble sulfate instead of sulfuric acid.

The addition of a little silver nitrate to an aqueous solution of barium chloride causes the formation of a white, curdy precipitate of silver chloride which darkens on exposure to light:

$$BaCl_2 + 2AgNO_3 = Ba(NO_3)_2 + 2\ \mathbf{AgCl}.$$

The same precipitate is formed when hydrochloric acid or any other chloride is used instead of the barium chloride and when any other soluble silver salt is used instead of silver nitrate.

In the same way there are certain properties which are shown by aqueous solutions of all acids. Blue litmus is turned red, carbonates are decomposed with effervescence, and metals are dissolved. These so-called *acid properties* are due to the hydrogen of acids, which behaves in an essentially different manner than the hydrogen of other compounds.

Bases also show certain characteristic reactions which can be traced to the hydroxyl, OH, that they contain. An aqueous solution of a base turns red litmus blue and reacts with the hydrogen of an acid to form water.

The aqueous solutions of acids, bases and salts, therefore, show reactions which are characteristic not so much of the dissolved substance as a whole as of its constituents. This is a very important point. It enables us to test for the constituents of a solution more or less independently of what other constituents may be present. We can test for barium in just the same way whether it is present as chloride or as nitrate, and we can test for chlorine by the same reagent no matter whether the chlorine was originally present as hydrochloric acid or as some other chloride. This is quite remarkable, because the chemical properties of a compound are usually quite different from the sum of the properties of its constituents. The properties of the chemical compound water show little similarity to the properties of either hydrogen or oxygen gas. The properties of sodium iodide are quite different from those of metallic sodium and of free iodine, and those of potassium chlorate are quite distinct from the properties of the potas-

sium, chlorine and oxygen which it contains. Aqueous solutions of acids, bases and salts, however, actually do show additive properties, i.e., sodium chloride in solution shows properties which the sodium of any other sodium salt will show, plus other properties which any other chloride will show. This suggests the hypothesis that the aqueous solution of an acid must contain the acid hydrogen, to some extent at least, in the same condition as in the aqueous solution of any other acid; that an aqueous solution of a base must contain a part at least of its hydroxyl in the same condition as the aqueous solutions of any other base; and that the metals and non-metals of salts must be present in very much the same condition irrespective of the nature of the original salt. This would mean that when the acid, the base, or the salt is dissolved in water, it is decomposed to some extent into smaller units.

Not only the chemical but also the physical behavior of aqueous solutions of acids, bases and salts indicates that the constituents are present in a condition such that they may react independently. The boiling-point of a solution of sugar in water is higher and its freezing-point lower than that of pure water. It has been found that the rise in boiling-point and lowering of the freezing-point is proportional to the number of molecules of dissolved substance present. This rule holds so exactly for solutions of organic substances dissolved in organic solvents that it serves for the determination of molecular weights. When, however, it is attempted to determine the molecular weight of an acid, a base, or a salt, by determining the boiling-point or the freezing-point of its aqueous solution, it is found that the molecular weight thus found is always too small. In other words, a study of the boiling-point or freezing-point of acids, bases and salts indicates that the original molecules of the acid, base or salt have been more or less split up into units smaller than the original molecule.

Finally the electrical behavior corroborates this view. It is well known that substances behave differently toward the electric current; some are conductors of it and others are non-conductors. Metals are good conductors and sulfur is a non-conductor. Again, the conductors are divided into two classes. Metals belong to the first class and conduct electricity without experiencing any change except that they become warmer. Conductors of the second class are chiefly aqueous solutions of acids, bases and salts. Simultaneous with the conduction of the current they undergo a chemical change, and decomposition products are obtained at each electrode.

Theory of Electrolytic Dissociation or Ionization

If we insert between the poles of an electric battery a piece of rock salt or some pure distilled water, there will be no electric current in the circuit; a piece of fine platinum wire placed in the circuit will not be made to glow. The solid rock salt and the distilled water are non-conductors of electricity; they are non-electrolytes. If, however, we dissolve rock salt in distilled water, and then insert the solution between the poles of the electric battery, the platinum wire will be brought to a bright glow, showing that the salt solution is a good conductor of electricity — it is an electrolyte. It is thereby proved that by dissolving the non-conducting rock salt in non-conducting water an essential change of the former has taken place. We can make the same observation with all acids, bases and salts. In an anhydrous state they are non-electrolytes, while in aqueous solution,* on the other hand, they are electrolytes. These phenomena are readily explained by the theory of electrolytic dissociation proposed by Arrhenius † in 1887. According to this theory, all electrolytes are partially decomposed in aqueous solution into electrically charged atoms or atom-groups called *ions;* and the extent of this ionization increases with dilution, until with very great dilution it is practically complete.‡ For every degree of dilution there exists a certain state of equilibrium between the ions and undissociated molecules.

When the non-electrolyte rock salt is dissolved in water, it breaks up, according to the equation

$$NaCl \rightleftarrows Na^+ + Cl^-,$$

into positively charged sodium ions and negatively charged chloride ions.§

---

* They are also electrolytes in the fused state.

† Z. phys. Chem., **1**, 631.

‡ There are exceptions to the general rule that ionization increases with the dilution. Sodium chloride, for example, appears to be incompletely ionized in an aqueous solution containing about 60 grams per liter but the extent of the ionization increases upon concentrating the solution as well as upon diluting it. A concentrated solution of sodium chloride as well as a very dilute one apparently contains the salt in a completely ionized state. Cf. NOYES and MACINNES, *J. Am. Chem. Soc.*, **42**, 239 (1920); LATIMER and RODEBUSH, *Ibid.*, **42**, 1423 (1920).

§ Many chemists prefer to designate the positive ions by small dots and the anions by small inclined dashes. The above equation is then written: $NaCl \rightleftarrows Na^{\cdot} + Cl'$.

Nearly all salts, acids and bases behave like rock salt. Thus sodium sulfate decomposes according to the equation

$$Na_2SO_4 \rightleftarrows Na^+ + Na^+ + SO_4^{--},$$

and sodium hydroxide into

$$NaOH \rightleftarrows Na^+ + OH^-.$$

By this theory of electrolytic dissociation the phenomena of electrolysis may be explained very simply: If we insert the two poles of a source of electricity into an electrolyte, one of the poles, the anode, is charged with positive electricity, and the other, the cathode, with negative electricity. The electro-positive anode repels the electro-positive ions (cations) and attracts the electronegative ions (anions); and the latter, as soon as they come in contact with the anode, give up their negative electricity, become neutral and separate out.* The same thing happens at the cathode, where the electro-positive ions (cations) are discharged. The quantities of electricity which are neutralized at the electrodes are always renewed by the source of the current, so that the process is continuous.

The electric charge on one atomic weight in grams of a univalent ion is 96,500 coulombs; † on an atomic weight in grams of a bivalent ion the charge is twice as much, and on a trivalent ion three times as much. To deposit one atomic weight in grams of silver at the cathode, therefore, it is necessary for 96,500 coulombs of electricity to pass through the solution, and there will be a simultaneous discharge of an equivalent weight of anion at the anode. One coulomb is the quantity of electricity which is represented by the flow of 1 ampere for one second; 96,500 coulombs, therefore, represent 96,500 ampere seconds or 26.8 ampere hours.

The transport of electricity in aqueous solutions takes place only by means of the ions; the undissociated molecules take no part in the process. The concentration of the ions and the conductivity of the solution are quantities which are proportional to one another. It is possible, therefore, to determine the extent to which a solution is

* The ion that carries the current from one electrode to the other is not always discharged at its destination. Sometimes it reacts with the electrode which dissolves and sometimes it is easier to set free hydrogen and oxygen from water than it is to discharge the ion that carried the current. Thus, in the electrolysis of sodium chloride solution, there is no sodium formed at the cathode, except when the latter consists of mercury, because it is easier to set free hydrogen from water than to discharge sodium ions. If any free sodium were formed it would at once react with water. With a mercury cathode, however, sodium amalgam may be formed.

† This quantity of electricity is called *one Faraday*. The value as given is accurate for three significant figures only.

dissociated into its ions by measuring the electrical conductivity of the solution.

The laws governing electrolysis were well understood by Michael Faraday in 1834, and he gave the name of *ions* to those parts of the solution which migrate toward the electrodes (cf. p. 10). The positive electrode is called the *anode* and the negatively charged *ion* which is attracted toward it is called the *anion;* the negative electrode is called the *cathode* and the positively charged ion which is attracted toward it is called the *cation.* In Faraday's time it was thought that the first action of the electric current was to decompose the molecules of the substance into the ions. About 1885 Arrhenius made the simple observation that all those solutions in which the dissolved substances have abnormally low molecular weights, as determined by boiling-point elevation, by freezing-point lowering, or by some similar method, are solutions which permit the passage of the electric current — they are *electrolytes;* while solutions which give normal results in the determination of the molecular weight of the dissolved substances are *non-electrolytes.* Since 1885, therefore, it has been believed by most chemists that electrolytic dissociation, or ionization, takes place when an acid or a base or a salt dissolves in water.

This accounts for the fact that aqueous solutions of all silver salts show similar reactions. They all contain the silver cation, and the silver cation is different from ordinary metallic silver chiefly on account of the fact that it bears a large electric charge. Most of the reactions of qualitative analysis are carried out in aqueous solutions with electrolytes. Most of the separations employed and most of the tests are by means of reactions which are characteristic of the ions. For this reason, a proper understanding of the theory of electrolytic dissociation is necessary in the study of qualitative analysis.

Let us interpret the action of a *dilute* solution of an acid upon a *dilute* solution of a base. In a dilute solution of hydrochloric acid, for example, the hydrogen chloride is almost completely ionized, and in a dilute solution of sodium hydroxide the base is also almost completely ionized. Hydrochloric acid and sodium hydroxide react to form water, which is itself but very slightly ionized. The reaction between the dilute solutions of hydrochloric acid and sodium hydroxide may be written:

$$H^+ + Cl^- + Na^+ + OH^- = H_2O + Na^+ + Cl^-.$$

By subtracting the ions which appear on each side of the equality sign, the equation becomes:

$$H^+ + OH^- = H_2O.$$

According to this, the neutralization of a *dilute* solution of an acid by a base is merely the reaction of hydrogen ions with hydroxyl ions to form undissociated water. This is known to be true, because if the reaction takes place with 1 gm. of hydrogen and 17 gms. of hydroxyl the heat evolved is 13,700 calories. This same amount of heat is evolved when an equivalent amount of a dilute solution of hydrochloric acid is neutralized by a dilute solution of potassium hydroxide, or when the hydrochloric acid is replaced by another acid such as nitric acid; it represents merely the heat of formation of a molecular weight in grams (one *mole*) of water from hydrogen ions and hydroxyl ions.

Similarly it can be shown that when an acid acts on a metal with the formation of a salt and liberation of hydrogen gas, the quantity of heat which is developed depends only on the nature of the metal and is independent of the acid. The anion of the acid really does not take part in the reaction at all.

The main assumptions of the Arrhenius theory of electrolytic dissociation are as follows: When an acid, a base or a salt dissolves in water its molecules are immediately dissociated to some extent into smaller fragments called ions. These ions are charged with electricity. The sum of the positive charges residing on the cations is exactly equal to the sum of the negative charges residing upon the anions and the whole solution is electrically neutral. The dissociation is a reversible reaction and all electrolytes may be considered to be completely ionized at infinite dilution. Except for the dependence resulting from the electrical charges and the consequent attractions and repulsions between ions, the ions may be regarded as independent constituents with individual and specific chemical and physical properties. If a substance dissolves in water and is only partly dissociated, then when the ions are removed, either by electrolysis or as a result of chemical reaction, the substance will at once continue to form ions.

While it is true that most inorganic acids, bases and salts are *ionogens*,* yet the extent to which ionization takes place when the substance is dissolved in water varies greatly. Thus a molecular weight in grams of hydrogen chloride dissolved in 10 liters of water yields about seventy times as many hydrogen ions as an equivalent quantity of acetic acid; a similar comparison can be made with regard to sodium hydroxide solution and ammonium hydroxide. Since the *strength* of

* An *ionogen*, as its name indicates, is a substance capable of forming ions; According to the valence theory of G. N. LEWIS (*J. Am. Chem. Soc.*, **36**, 762 (1916); cf. LANGMUIR, *ibid.*, **41**, 868, 1543 (1919), an ionogen is a *polar* compound in which the valence electron has passed from one atom to another forming, when only two atoms are involved, an electric dipole.

an acid is determined by the degree of ionization, hydrochloric acid is about seventy times as strong an acid as acetic acid and sodium hydroxide or potassium hydroxide is nearly seventy times as strong a base as ammonium hydroxide.

On the other hand, a molecular weight of acetic acid will neutralize the same weight of sodium hydroxide that a molecular weight of hydrochloric acid does, and a molecular weight of ammonium hydroxide will neutralize the same weight of acid that a molecular weight of sodium hydroxide does. In a solution of sodium hydroxide and of hydrochloric acid of the above concentration the original molecules are about 90 per cent ionized, and when the acid and base are mixed the principal change is the union of hydrogen ions and hydroxyl ions to form water. When acetic acid of the same concentration is used, there is present at the start only 1.3 per cent of all the hydrogen in the form of ions. These ions will at once react with hydroxyl ions to form water, but there is always a tendency for the acetic acid to ionize, and when the ions disappear as fast as they are formed the ionization continues until all the molecules of acetic acid have dissociated. In the neutralization of acetic acid with sodium hydroxide, the final heat effect will not be simply that of the union of hydrogen ions with hydroxyl ions, but will also involve the energy required to cause the acetic acid to ionize. When a substance ionizes as soon as it dissolves, the heat effect of ionization cannot easily be distinguished from the heat of solution. Just as some substances dissolve with absorption of heat and some with evolution of heat, so it is found that the ionization process may likewise be associated with either an absorption or evolution of heat.

It is interesting to note, and this is a matter of considerable importance, that the salts of weak acids and of weak bases are usually ionized nearly as much as the salts of strong acids or of strong bases.

When a dibasic acid dissolves in water, the two hydrogen atoms do not ionize to an equal extent The ionization takes place in two stages. Thus with sulfuric acid the first stage takes place in the sense of the equation:

$$H_2SO_4 \rightleftarrows H^+ + HSO_4^-.$$

The fact that the reaction does not necessarily take place completely is indicated by using the double arrow sign instead of the equality sign. When the above reaction stops there is a state of equilibrium between the three substances H_2SO_4, H^+ and HSO_4^-. The HSO_4^- undergoes a secondary ionization as follows:

$$HSO_4^- \rightleftarrows H^+ + SO_4^{--}.$$

The extent to which these reactions takes place depends entirely upon the dilution. If half a molecular weight in grams of sulfuric acid is dissolved in 10 liters of water, the primary ionization will take place to about 90 per cent of the entire quantity of acid present and the secondary ionization to less than 50 per cent. If the solution is extremely dilute, both reactions will take place almost completely.

In the case of carbonic acid, the primary stage

$$H_2CO_3 \rightleftarrows H^+ + HCO_3^-$$

ordinarily takes place only to a fraction of 1 per cent and the second stage

$$HCO_3^- \rightleftarrows H^+ + CO_3^{--}$$

to an inappreciable extent (cf. p. 10). With hydrogen sulfide the relations are similar.

On the other hand, the salts of these weak acids will ionize almost completely as follows:

$$Na_2CO_3 \rightleftarrows Na^+ + Na^+ + CO_3^{--}$$
$$Na_2S \rightleftarrows Na^+ + Na^+ + S^{--}.$$

The fact that the extent to which a substance ionizes is dependent upon the concentration of the solution has already been indicated (p. 4) and will be demonstrated mathematically a little farther on (p. 18). The concentration of a solution shows the quantity of dissolved substance present in a unit volume, and the numerical value representing this concentration depends entirely upon the units in which the mass of the dissolved substance and the volume of the solution are expressed. If w represents the mass of dissolved substance in grams and v is the volume of the solution expressed in liters, then $\frac{w}{v}$ is the concentration of the solution in grams per liter. Concentrations are often expressed in these units, but the weight is not the most convenient unit for expressing the mass, especially in matters of theoretical discussion. A solution containing 1 gm. of dissolved substance A is rarely equivalent to one containing the same weight of a substance B. It is much more convenient to measure the mass of the dissolved substance in terms of the number of molecules present. According to the suggestion of Ostwald, the term *mole* has been given to the molecular weight of a substance in grams, and when the concentration of a solution is expressed in the number of moles present in a liter, the so-called *molal* concentration is obtained. The objection still remains, however, that one molecule of a substance A (e.g., hydrochloric acid) is not always equivalent to one molecule of a substance B (e.g., sulfuric acid). To overcome this difficulty, concentrations are often expressed in *gram equivalents* per liter, using

the univalent substances as the standard. Thus a mole of hydrochloric acid is one equivalent weight in grams and half a mole of sulfuric acid is one equivalent weight in grams. A solution which contains one equivalent weight in grams of dissolved substance is called a *normal solution;* one containing two equivalents in a liter is a twice-normal solution; and one containing half an equivalent is a half-normal solution. In analytical chemistry this is often the best way to express concentrations.

The following table will be found useful in studying the ionization of electrolytes. It gives the approximate percentage ionization of substances present in 0.1 N solution at 25° C. In the case of polybasic acids, the value opposite the formula of the acid shows the fraction of the whole molecule which undergoes the primary ionization into one hydrogen ion, that opposite an ion with a univalent charge shows the extent to which this ion undergoes a secondary ionization, and that opposite an ion with a bivalent charge shows the extent to which it undergoes a tertiary decomposition, forming a third hydrogen ion from the original neutral molecule of the acid.

Ionization Values of Common Electrolytes

In 0.1 normal solution	Per Cent
Salts of the type B^+A^- (e.g., KNO_3)*	84
Salts of the type $B_2^+A^{--}$ or $B^{++}A_2^-$ (e.g., K_2SO_4 or $BaCl_2$) †	73
Salts of the type $B_3^+A^{---}$, or $B^{+++}A_3^-$ (e.g., $K_3[Fe(CN)_6]$ or $AlCl_3$)	65
Salts of the type $B^{++}A^{--}$ (e.g., $MgSO_4$)	40
KOH, NaOH*	90
$Ba(OH)_2$*	80
NH_4OH	1.3
HCl, HBr, HI, HSCN, HNO_3, $HClO_3$, $HClO_4$, H_2SO_4, H_2CrO_4*	90
H_3PO_4, H_3AsO_4, H_2SO_3, $H_2C_2O_4$, HSO_4^-	20–45
HNO_2, HF	7–9
$HC_2H_3O_2$, $HC_2O_4^-$, HSO_3^-	1–2
H_2S, H_2CO_3, $H_3PO_4^-$, $HCrO_4^-$	0.1–0.2
HBO_2, $HAsO_2$, HCN, HCO_3^-, HClO	0.002–0.008
HS^-, HPO_4^{--}, $HAsO_4^{--}$	0.0001–0.0002
HOH (at 25°)	0.00,000,02

Nomenclature of the Ions

As already mentioned (p. 5) Faraday in 1834 was the first to use the words *ion, cathode, cation, electrode, anode,* etc. These names are all derived from Greek roots. Faraday's idea was that the electricity entered the solution at the positive pole and passed *down* to the

* These values are based upon electrical conductance ratios and are probably too low. Cf. page 46.

† Exceptions: $CdCl_2$ ionizes to about 47 per cent, $HgCl_2$ to about 0.01 per cent, and $HgBr_2$, HgI_2, and $Hg(CN)_2$ less than $HgCl_2$.

negative pole. The word *ion* is the Greek word for *wanderer* or *traveler* spelt in Latin letters. Anode is from the Greek ἀνά (ana) up; ὁδός (odos) a path. Cathode is from the Greek κατά (kata) down; ὁδός (odos) a path. The two electrodes are considered as the doors or paths by which the current enters and passes out of the solution.

Two methods are in common use for designating the ions. Thus the ions of hydrochloric acid are designated as H^+ and Cl^- or as H· and Cl′. Small plus and minus signs are used in this book rather than the dots and dashes simply because this is the present practice in the journals published by the American Chemical Society. Many writers prefer to use the other system because it takes up less room; in the case of the polyvalent ions the use of the plus and minus signs is often very cumbersome.

Purely as a matter of convenience, an attempt has been made to devise a system of rational nomenclature for the ions. This method has been adopted in a number of excellent text-books but it is not in common use. According to this system, the names of the cations are obtained by adding the termination *-ion* to the stem of the name of the corresponding metal, using the Latin name whenever possible. When a substance forms several ions differing from one another only in valence, the names of such ions are designated by Greek prefixes indicating the number of charges residing on the ion. The names of the anions are derived from the names of the salts. If the name of the salt ends in *-ate*, these last three letters are replaced by the ending *-anion*, except in the case of the carbonate ion, which is called *carbanion*. The names of anions from salts ending in *-ite* are formed by replacing these three letters with *-osion*. The anions from salts whose names end in *-ide* are obtained by replacing these letters with the ending *-idion*. The hydrogen ion is called *hydrion* and the hydroxyl ion is called *hydroxidion*. The following table illustrates the use of this system which was proposed by Walker:

NAMES OF CERTAIN IONS

Symbol.	Name.	Cation of Salts of	Symbol.	Name.	Anion of
Ag^+	Argention	Silver	Cl^-	Chloridion	Chlorides
Ca^{++}	Calcion	Calcium	ClO^-	Hypochlor-osion	Hypochlorites
Cu^{++}	Dicuprion	Cupric copper			
Fe^{++}	Diferrion	Ferrous iron	ClO_2^-	Chlorosion	Chlorites
Fe^{+++}	Triferrion	Ferric iron	ClO_3^-	Chloranion	Chlorates
H^+	Hydrion	Hydrogen (Acids)	ClO_4^-	Perchloranion	Perchlorates
			S^{--}	Sulfidion	Sulfides
K^+	Kalion	Potassium	SO_3^{--}	Sulfosion	Sulfites
Na^+	Natrion	Sodium	SO_4^{--}	Sulfanion	Sulfates
NH_4^+	Ammonion	Ammonium	NO_3^-	Nitranion	Nitrates
			OH^-	Hydroxidion	Hydroxides (Bases)

Equilibrium between a Solid and a Liquid

Most of the reactions used in analytical chemistry involve either the solution or the precipitation of some substance. It is important, therefore, to consider briefly the relations which exist between a solid and its solution.

Potassium nitrate on being brought into contact with water at once begins to dissolve. The rate of solution is influenced somewhat by the amount of surface exposed by the salt, a fine powder dissolving more rapidly than a single large crystal. At first the substance dissolves quite rapidly, particularly if the liquid is kept stirred, but gradually the speed slackens and finally a time comes when the water at a given temperature will dissolve no more of the salt. The solution is then said to be *saturated* with the salt and it makes no difference how much potassium nitrate is available in excess of the amount required to form a saturated solution, the solution when once saturated at any temperature will dissolve no more salt.

The quantity of salt required to form a saturated solution varies with the temperature, more so with potassium nitrate than with many other salts. At 0° the saturated solution contains only 1.3 moles of potassium nitrate, whereas 2.7 moles dissolve at 20° and 25 moles dissolve at 100°.

If a solution containing 5 moles of potassium nitrate is prepared by dissolving the salt in hot water and the solution is then cooled to 20°, we obtain what is called a *supersaturated* solution. A state of supersaturation can be maintained for some time provided care is taken not to disturb the solution in any way. If the supersaturated solution is agitated, or, better, if a tiny fragment of potassium nitrate is thrown into it, crystallization starts and continues until finally the solution only contains 2.7 moles of the salt, which is the quantity of potassium nitrate required to form a saturated solution at 20°.

The solubility of a substance at any temperature is usually determined by two methods: first, by shaking up the salt with water until a saturated solution is obtained; second, by forming a supersaturated solution and allowing the excess of the salt to crystallize out. Usually the values obtained by the former method are a little lower than the values obtained by the latter method; a slightly undersaturated solution is obtained in one case and a slightly supersaturated one in the other.

When a solution of potassium nitrate is brought into contact with more of the salt, whether more of the salt will dissolve or not is determined solely by the concentration of the solution. If it is

already saturated with potassium nitrate, no more of the salt will dissolve; if unsaturated, more salt will dissolve to form a saturated solution. The equilibrium between a liquid and a solid which is soluble in it is determined solely by the concentration of the solution. The absolute quantity of substance and the absolute quantity of solution have no effect upon the final equilibrium.

Chemists prefer to look upon a state of equilibrium as a condition of dynamic equilibrium rather than as one of static equilibrium. Instead of thinking of the saturated solution of potassium nitrate as one which has no tendency to dissolve more potassium nitrate, it is preferable to consider the solution as one in which the tendency to precipitate potassium nitrate is exactly balanced by the tendency to dissolve potassium nitrate. When the solution is undersaturated and more salt is available, the tendency to dissolve is greater than the tendency to precipitate and when the solution is supersaturated the tendency to precipitate is greater than the tendency to dissolve.

The equilibrium principle is the same in the case of difficultly soluble substances. It requires only 0.0015 gram (= 0.01 millimole) of silver chloride to form a saturated solution in water. If more than this quantity of silver chloride is produced as a result of a chemical reaction taking place in an aqueous solution, all the excess silver chloride will be precipitated. The solubility is so slight that the precipitation is practically complete.

Chemical Equilibrium and the Mass Action Law

If hydrogen sulfide gas is passed into a solution containing zinc chloride, a white precipitate of zinc sulfide is formed:

$$ZnCl_2 + H_2S = ZnS + 2HCl.$$

If the precipitate of zinc sulfide is filtered off and treated with hydrochloric acid it will dissolve:

$$ZnS + 2HCl = ZnCl_2 + H_2S.$$

Similarly, the addition of ammonium carbonate to a solution of calcium chloride in water causes the formation of a white precipitate of calcium carbonate:

$$CaCl_2 + (NH_4)_2CO_3 = CaCO_3 + 2NH_4Cl.$$

The precipitate can be dissolved, however, by boiling it with ammonium chloride solution.

In each of the above cases, there are evidently two opposing tendencies — the tendency of zinc sulfide to precipitate and the tendency of zinc sulfide to dissolve; the tendency of calcium carbonate

to precipitate and the tendency of calcium carbonate to dissolve. To express the fact that the reaction may go in either direction it is customary to write the symbols separated by a double arrow instead of by an equality sign (cf. p. 8):

$$ZnCl_2 + H_2S \rightleftarrows \mathbf{ZnS} + 2HCl,$$
$$CaCl_2 + (NH_4)_2CO_3 \rightleftarrows \mathbf{CaCO_3} + 2NH_4Cl.$$

Such reactions are called *reversible*. It was once thought that reversible reactions were of rare occurrence, but it is now customary to consider all chemical reactions as reversible, although in many cases, and especially in most reactions used in analytical chemistry, the reaction goes so completely in one direction that only a negligible quantity of one or more of the initial substances remains unchanged. In general, when two substances A and B react at a constant temperature to form C and D, then, to some extent at least, C and D react to form A and B, and equilibrium is reached when the ratio of the product of the concentrations of A and B to the product of the concentrations of C and D has a definite, constant value. This value is characteristic of the equilibrium between the compounds involved.

In the above case, the reaction may be expressed as follows:

$$A + B \rightleftarrows C + D,$$

in which A, B, C and D represent four different substances reacting in the molecular proportions indicated by their symbols. The final equilibrium is expressed by the mathematical equation:

$$\frac{[C] \times [D]}{[A] \times [B]} = k,$$

in which $[A]$, $[B]$, $[C]$ and $[D]$ represent the final concentrations * of the four reacting substances and k is some definite number called the equilibrium constant. The value k varies with the temperature.

If more than one molecule of substance takes part in the reaction, the conditions are somewhat more complicated. This is expressed by the general equation

$$mA + nB \rightleftarrows pC + qD$$

and the final equilibrium is expressed mathematically

$$\frac{[C]^p \times [D]^q}{[A]^m \times [B]^n} = k,$$

in which $[A]$, $[B]$, $[C]$ and $[D]$ represent, as before, the concentrations when equilibrium is reached.

This is the so-called *law of mass action*, which was discovered by

* Concentrations in such cases are usually expressed in *moles per liter*.

Guldberg and Waage in 1867. It is to be noted that it is the concentrations, or masses present in a unit of volume, rather than the actual masses of the substances, which find expression in this law.

This law applies to a state of *homogeneous equilibrium.* A homogeneous system is one in which every part of it is like every other part. A mixture of two solid substances is not homogeneous. A solution, on the other hand, is homogeneous when it is thoroughly mixed, as it is impossible to distinguish any difference between different portions of the solution. Similarly a mixture of gases represents a homogeneous system. Such homogeneous systems are called *phases.* A mixture of a solid, a solution and a gas represents three phases; two solids, two phases; two immiscible liquids, two phases.

In the case of the reactions between zinc chloride and hydrogen sulfide and between calcium chloride and ammonium carbonate a precipitate was formed in each case. The mass-action law applied only to the zinc sulfide and to the calcium carbonate that remained in solution.* The fact that these substances are only very slightly soluble in water favors the progress of the reaction in the direction by which these substances are formed. The mass-action law shows that when the concentration of any substance participating in a chemical reaction is increased, this tends to increase the tendency for the reaction to take place in the direction by which this substance is decomposed; when any substance formed by means of a chemical reaction is removed this increases the tendency for the reaction to proceed in the direction by which this substance is formed. The formation of a precipitate or the escape of a gas, as fast as the substance is formed by means of a chemical reaction, tends to make the reaction take place more completely. If the gas is all boiled off the reaction by which it is formed will take place completely. Similarly if any precipitate were absolutely insoluble in water, the reactions by which this substance is formed would take place completely.

This law of mass action embodies one of the most important principles utilized in analytical chemistry. It enables one to understand why most of the reactions take place and to establish conditions under which these reactions will occur to the best advantage. The law has been verified by a great many quantitative as well as qualitative experiments. It has been studied, for example, in connection with the formation and decomposition of phosphorus pentachloride.

When chlorine gas reacts with cold phosphorus trichloride, the solid

* The mass action law is concerned with the *concentrations* of the reaction substances. The quantity of zinc sulfide or calcium carbonate that remains dissolved to form a saturated solution is independent of the quantity of precipitate formed.

pentachloride is formed; but if this substance is heated, it breaks down into its constituents. The reaction is reversible and may be expressed as follows:

$$PCl_5 \rightleftarrows PCl_3 + Cl_2.$$

At any given temperature an equilibrium exists which can be expressed mathematically, according to the mass-action law,

$$\frac{[PCl_3] \times [Cl_2]}{[PCl_5]} = k,$$

in which $[PCl_3]$, $[Cl_2]$ and $[PCl_5]$ represent the concentrations at the time when equilibrium has been reached.

If we desire to volatilize phosphorus pentachloride so that the least possible dissociation will take place, the above equation shows us how this may be brought about.

If either $[PCl_3]$ or $[Cl_2]$ be increased, then in order that the value of the fraction

$$\frac{[PCl_3] \times [Cl_2]}{[PCl_5]}$$

remains constant, it is evident that the concentration $[PCl_5]$ must become greater; or, in other words, the dissociation of the pentachloride becomes less and there will be practically no dissociation if the pentachloride is volatilized in an atmosphere of phosphorus trichloride or of chlorine. In this way, Wurz obtained for the density of phosphorus pentachloride 6.80–7.42, instead of the calculated value 7.2.

At Stassfurt the mineral carnallite ($MgCl_2 \cdot KCl \cdot 6H_2O$) occurs and was evidently formed by precipitation from solutions containing the chlorides of magnesium and potassium. This double salt is less soluble than pure magnesium chloride and more soluble than pure potassium chloride. If carnallite is dissolved in water and the solution allowed to evaporate until crystals are deposited, it will be found that the crystals consist of potassium chloride. When the carnallite dissolves in water, the double salt is decomposed, more or less completely according to the dilution,

$$MgCl_2 \cdot KCl \rightleftarrows MgCl_2 + KCl,$$

and for every concentration the equation holds:

$$\frac{[MgCl_2] \times [KCl]}{[MgCl_2 \cdot KCl]} = \text{a constant.}$$

If we wish to recrystallize the carnallite, the breaking down of the double salt must be prevented as much as possible, and to do this it is

merely necessary to add an excess of $MgCl_2$. As a matter of fact, the mineral is recrystallized at Stassfurt from a 23 per cent solution of magnesium chloride.

This law of mass-action applies to all cases of chemical equilibrium that takes place in a homogeneous phase, i.e., it can be applied to all reactions which take place between gases and to all reactions that take place in solution.

The law of mass action applies to the equilibrium between an ionogen and its ions. In this connection, the law is of particular importance in the study of analytical chemistry.

Equilibrium between a Solid and Two Liquids

Although water, either pure or containing dissolved acid, is the solvent most used in analytical chemistry, it often happens that a substance is more soluble in some other liquid. Thus free iodine is about 400 times as soluble in carbon disulfide as it is in water. When iodine is in contact with both carbon disulfide and water, and these two liquids are only slightly soluble in one another, it will dissolve chiefly in the carbon disulfide. Moreover, if an aqueous solution of iodine is shaken with carbon disulfide, the latter, when it separates out beneath the water, will contain nearly all of the iodine. A state of equilibrium then exists between the solution of iodine in water and the solution of iodine in carbon disulfide. Such an equilibrium is governed by the so-called *distribution law* or *law of partition*. If C_A represents the concentration of a substance in a solvent A and C_B is its concentration in a solvent B, equilibrium is reached when

$$\frac{C_A}{C_B} = k.$$

This is the mathematical expression of the distribution law. The constant, k, is called the *distribution coefficient*. In this simple form, it is important to note that the law holds only when each concentration is expressed in terms of the same molecular species. Thus if a substance is dissociated to a large extent in one solvent and scarcely at all in another, the concentrations involved must be those of the undissociated salt in each case. It is quite common to find that the *ions* of a substance are much more soluble in water than in any other solvent whereas for the undissociated substance the relations are reversed. Iodine dissolves to a greater extent in a solution of potassium iodide than it does in pure water, owing to the formation of KI_3. In such a solution the following equilibrium exists:

$$KI + I_2 \rightleftarrows KI_3.$$

If such a solution is shaken with carbon disulfide, the distribution law holds only for the free iodine held in solution as such in each solution.

For iodine in pure water and iodine in carbon disulfide, the distribution coefficient is $\frac{1}{100}$. Theoretically it is impossible to remove all the iodine from water by shaking with carbon disulfide, but if the carbon disulfide is removed, with the aid of a separatory funnel, and the aqueous solution is shaken with fresh carbon disulfide, it is evident that the quantity of iodine remaining with the water is negligible, or can be made so by repeating the operation.

Sometimes in testing for the halides it is desirable to remove free halogen from the aqueous solution; to accomplish this, the distribution principle is utilized. Ferric chloride is much more soluble in ether and hydrochloric acid than it is in water and hydrochloric acid; to detect the minor constituents of iron or steel, a large sample of the original material is taken and the ferric chloride removed by shaking the hydrochloric acid solution with ether. Perchromic acid is more soluble in ether than it is in water; by shaking the dilute aqueous solution with a little ether, a concentrated solution in the latter is obtained and the presence of the chromium shown by the beautiful blue color.

Influence of Changes in Concentration upon the Ionization of Electrolytes

If we assume 1 mole of a weak electrolyte, such as ammonium hydroxide, to be dissolved in v liters of solution, the original substance will be partly ionized according to the equation

$$NH_4OH \rightleftarrows NH_4^+ + OH^-$$

into ammonium and hydroxyl ions. If α is the fraction of the base ionized in the sense of the above equation, then the non-ionized part will amount to $1 - \alpha$.

The concentrations per liter are

$$NH_4OH \rightleftarrows NH_4^+ + OH^-$$

$$\frac{1-\alpha}{v} \qquad \frac{\alpha}{v} \qquad \frac{\alpha}{v}$$

and according to the *mass-action* law

$$k \cdot \frac{1-\alpha}{v} = \frac{\alpha^2}{v^2}$$

$$k = \frac{\alpha^2}{(1-\alpha)v}.$$

The constant k is known as the *ionization-* or *affinity-constant;* it is independent of the dilution and is characteristic for every electrolyte. The expression shows, however, that by increasing v, or diluting, the fraction of the molecule dissociated (α) will be made larger.

If to the solution of the base we add n additional ammonium ions, by adding solid ammonium chloride, then if n is considerably larger than α the degree of ionization of the base will be greatly diminished, namely, from α to α_1, a value which can be readily computed as follows:

In the solution there is present per liter

$$NH_4OH \rightleftarrows NH_4^+ + OH^-$$

$$\frac{1-\alpha_1}{v} \quad \frac{\alpha_1+n}{v} \quad \frac{\alpha_1}{v},$$

therefore

$$k = \frac{(\alpha_1+n)\,\alpha_1}{(1-\alpha_1)\,v}.$$

If k and n are known, α_1 can be computed:*

$$\alpha_1 = \frac{-(n+vk) \pm \sqrt{(n+vk)^2+4vk}}{2}.$$

In the case of 0.1 N ammonia solution the ammonium hydroxide is ionized only to an extent of 1.32 per cent, the ionization constant being 0.000018. If we add to 10 liters of this ammonia solution 2 moles of ammonium chloride (107.08 gms.), then since the ammonium chloride is 93 per cent dissociated at this dilution, we are adding $2 \times 0.93 = 1.86\ NH_4^+$ ions. If this value be inserted in the above equation, α_1 becomes 0.00009; in other words, the ionization of the ammonium hydroxide is diminished by the addition of the ammonium chloride from 1.32 to 0.009 per cent. The solution now contains so few hydroxyl ions that it will not cause precipitation in solutions of magnesium salts (cf. pp. 46, 94).

Similarly the ionization of weak acids is lessened by the addition of their salts. In the case of the stronger acids and bases, the effect of adding a neutral salt to the solution is not so remarkable, because the stronger acids and bases are dissociated to about the same extent as their salts.

* Such computations rarely give information concerning ionization which is accurate to more than two significant figures. When α_1 is small (less than 0.01) the expression $k = \frac{(\alpha_1+n)\,\alpha_1}{(1-\alpha_1)\,v}$ may be simplified into $k = \frac{\alpha_1 n}{v}$ and it is then easy to compute the value of α_1. In most cases it is not only unnecessary but absurd to attempt to use the formula without approximation.

Solubility Product

Silver chloride is slightly soluble in water; 0.00001 mole (1.5 mgs.) of the solid dissolves in 1 liter of the solvent. When water is placed in contact with an excess of silver chloride, a state of equilibrium is soon reached between the solid and the solution. If more than this quantity of dissolved substance is present at any time, the solution is supersaturated and tends to precipitate silver chloride; if less, then more silver chloride will be dissolved. When equilibrium is reached the tendency of the salt to precipitate is equal to the tendency of the salt to dissolve.

The dissolved silver chloride also exists in a state of equilibrium between the ionogen and the ions. This equilibrium apparently takes place almost instantly, whereas the equilibrium between the solid and the solution is established more slowly. For all concentrations of such a slightly soluble substance as silver chloride, it is fair to assume that the mass-action law holds rigidly. Applied to the reaction

$$AgCl \rightleftarrows Ag^+ + Cl^-$$

and denoting the concentration of non-ionized silver chloride as [AgCl], of silver ions as [Ag], and of chlorine ions as [Cl], the law is expressed as follows:

$$\frac{[Ag] \times [Cl]}{[AgCl]} = k.$$

In this equation k has a definite value, called the *ionization constant*, which varies with the temperature but has otherwise a definite value for every substance. When the solution is saturated with silver chloride the value of both numerator and denominator has reached the saturation value. If the value of [AgCl] is greater than corresponds to this saturation value, the solution is supersaturated and is no longer in equilibrium with undissolved solid. The value [AgCl] could be used for expressing the solubility of the substance, but it is often more convenient to use the ion concentration product [Ag] × [Cl] which is called the *solubility product*. In general, if the substance A_mB_n ionizes into mA and nB ions, the solubility product, S_p, is found by the following equation:

$$S_p = [A]^m \times [B]^n = k\,[A_mB_n],$$

in which k is the ionization constant and the concentrations are those of a *saturated solution*.

Experience has shown that the conditions are somewhat more complicated in concentrated solutions such as are obtained with the very soluble substances. In future discussion, therefore, the solu-

bility will be expressed, as a rule, in terms of the solubility product only when the substance does not dissolve to a greater extent than 0.01 mole per liter. The table on page 10 shows that binary salts of the type represented by AgCl are ionized to about 84 per cent in 0.1 N solution, and we have seen on page 19 that the ionization increases as the solution is diluted. In the case of such a dilute solution as that of silver chloride (0.00001 normal) the ionization is nearly 100 per cent. It is therefore logical, in such cases, to express the solubility in terms of the ions, whereas in the case of the very soluble substances it is better to measure the solubility in terms of the mass of dissolved substance.

The numerical values of the ionization constant and of the solubility product depend upon the units used in measuring the mass of the dissolved substance or ions and in measuring the volume of the solution. It is customary, in this case, to express the concentration in moles per liter (cf. p. 9). In the following table the solubility of the substance is expressed in three ways: in grams of dissolved substance per liter, in moles per liter and, finally, in terms of the solubility product, using moles per liter. The solubility of most of the substances given in the table is so slight that the quantity dissolved is negligible for most purposes. Whenever the word *insoluble* is used in this book it is with the understood limitation that no substance is absolutely insoluble in water.

SOLUBILITIES AND SOLUBILITY PRODUCTS AT ROOM TEMPERATURE

Substance.	Solubility in Grams per Liter.	Solubility in Moles per Liter.	Solubility Product.
$AgBr$	1.1×10^{-4}	5.9×10^{-7}	$[Ag]\times[Br]=3.5\times10^{-13}$
$Ag_2(CN)_2$	4.3×10^{-5}	1.6×10^{-7}	$[Ag]\times[Ag(CN)_2]=2.6\times10^{-14}$
$AgCNS$	1.4×10^{-4}	8.4×10^{-7}	$[Ag]\times[CNS]=7.1\times10^{-13}$
$AgCl$	1.5×10^{-3}	1.1×10^{-5}	$[Ag]\times[Cl]=1.2\times10^{-10}$
Ag_2CrO_4	2.5×10^{-2}	7.5×10^{-5}	$[Ag]^2\times[CrO_4]=1.7\times10^{-12}$
$Ag_2Cr_2O_7$	8.3×10^{-2}	1.9×10^{-4}	$[Ag]^2\times[Cr_2O_7]=2.7\times10^{-11}$
Ag_2O	2.1×10^{-2}	9.0×10^{-5}	$[Ag]\times[OH]=1.9\times10^{-8}$
AgI	3.0×10^{-6}	1.3×10^{-8}	$[Ag]\times[I]=1.7\times10^{-16}$
$AgIO_3$	4.4×10^{-2}	1.5×10^{-4}	$[Ag]\times[IO_3]=2.3\times10^{-8}$
Ag_3PO_4	6.5×10^{-3}	1.6×10^{-5}	$[Ag]^3\times[PO_4]=1.8\times10^{-18}$
Ag_2SO_4	8.0	2.6×10^{-2}	$[Ag]^2\times[SO_4]=7.0\times10^{-5}$
$BaCO_3$	1.3×10^{-2}	4.3×10^{-5}	$[Ba]\times[CO_3]=1.9\times10^{-9}$
$BaCrO_4$	3.8×10^{-3}	1.5×10^{-5}	$[Ba]\times[CrO_4]=2.3\times10^{-10}$
$BaSO_4$	2.5×10^{-3}	1.1×10^{-5}	$[Ba]\times[SO_4]=1.2\times10^{-10}$
BaF_2	1.3	7.5×10^{-3}	$[Ba]\times[F]^2=1.7\times10^{-6}$
$CaCO_3$	1.3×10^{-2}	1.3×10^{-4}	$[Ca]\times[CO_3]=1.7\times10^{-8}$
CaC_2O_4	8.0×10^{-3}	6.2×10^{-5}	$[Ca]\times[C_2O_4]=3.8\times10^{-9}$
$CaCrO_4$	23.	1.5×10^{-1}	$[Ca]\times[CrO_4]=2.3\times10^{-2}$
CaF_2	1.6×10^{-2}	2.0×10^{-4}	$[Ca]\times[F]^2=3.2\times10^{-11}$

SOLUBILITIES AND SOLUBILITY PRODUCTS AT ROOM TEMPERATURE — *Continued*

Substance.	Solubility in Grams per Liter.	Solubility in Moles per Liter.	Solubility Product.
$CaSO_4$	2.0	1.5×10^{-2}	$[Ca]\times[SO_4]=2.3\times10^{-4}$
$Cu_2(CNS)_2$	5.0×10^{-4}	2.1×10^{-6}	$[Cu]\times[CNS]=1.7\times10^{-11}$
Cu_2Cl_2	1.2×10^{-1}	6.0×10^{-4}	$[Cu]\times[Cl]=1.4\times10^{-6}$
Cu_2I_2	3.0×10^{-4}	8.0×10^{-7}	$[Cu]\times[I]=2.6\times10^{-12}$
CuS	8.8×10^{-21}	9.2×10^{-23}	$[Cu]\times[S]=8.5\times10^{-45}$
CdS	8.6×10^{-13}	6.0×10^{-15}	$[Cd]\times[S]=3.6\times10^{-29}$
$Fe(OH)_2$	.....	.....	$[Fe]\times[OH]^2=1.6\times10^{-14}$
FeS	3.4×10^{-8}	3.9×10^{-10}	$[Fe]\times[S]=1.5\times10^{-19}$
$Fe(OH)_3$	.....	.....	$[Fe]\times[OH]^3=1.1\times10^{-36}$
Hg_2Br_2	3.9×10^{-5}	6.9×10^{-8}	$[Hg_2]\times[Br]^2=1.3\times10^{-21}$
Hg_2Cl_2	3.8×10^{-4}	8.0×10^{-7}	$[Hg_2]\times[Cl]^2=2.0\times10^{-18}$
Hg_2I_2	2.0×10^{-7}	3.1×10^{-10}	$[Hg_2]\times[I]^2=1.2\times10^{-28}$
HgO	.....	.....	$[Hg]\times[OH]^2=4.3\times10^{-16?}$
HgS	.....	.....	$[Hg]\times[S]=4.0\times10^{-53}$
K_2PtCl_6	11.	2.3×10^{-2}	$[K]^2\times[PtCl_6]=4.9\times10^{-5}$
$MgCO_3$	4.3×10^{-1}	5.1×10^{-3}	$[Mg]\times[CO_3]=2.6\times10^{-5}$
$Mg(OH)_2$	1.2×10^{-2}	2.0×10^{-4}	$[Mg]\times[OH]^2=3.4\times10^{-11}$
$MgNH_4PO_4$	8.6×10^{-3}	6.3×10^{-5}	$[Mg]\times[NH_4]\times[PO_4]=2.5\times10^{-13}$
$Mn(OH)_2$	.....	.....	$[Mn]\times[OH]^2=4.0\times10^{-14}$
MnS	3.3×10^{-6}	3.8×10^{-8}	$[Mn]\times[S]=1.4\times10^{-15}$
NiS least soluble allotropic form	7.0×10^{-11}	1.2×10^{-12}	$[Ni]\times[S]=1.4\times10^{-24}$
$PbBr_2$	9.7	2.7×10^{-2}	$[Pb]\times[Br]^2=7.9\times10^{-5}$
$PbCl_2$	11.	3.9×11^{-2}	$[Pb]\times[Cl]^2=2.4\times10^{-4}$
$PbCO_3$	1.1×10^{-3}	4.1×10^{-6}	$[Pb]\times[CO_3]=1.7\times10^{-11}$
PbI_2	6.8×10^{-1}	1.5×10^{-3}	$[Pb]\times[I]^2=1.4\times10^{-8}$
$Pb_3(PO_4)_2$	1.4×10^{-4}	1.7×10^{-7}	$[Pb]^3\times[PO_4]^2=1.5\times10^{-32}$
$PbSO_4$	4.2×10^{-2}	1.5×10^{-4}	$[Pb]\times[SO_4]=2.3\times10^{-8}$
$PbCrO_4$	4.3×10^{-5}	1.3×10^{-7}	$[Pb]\times[CrO_4]=1.8\times10^{-14}$
PbS	4.9×10^{-12}	2.0×10^{-14}	$[Pb]\times[S]=4.2\times10^{-28}$
SrC_2O_4	6.6×10^{-2}	3.8×10^{-4}	$[Sr]\times[C_2O_4]=1.4\times10^{-7}$
$SrCO_3$	1.0×10^{-2}	6.8×10^{-5}	$[Sr]\times[CO_3]=4.6\times10^{-9}$
SrF_2	2.3×10^{-1}	1.8×10^{-3}	$[Sr]\times[F]^2=2.5\times10^{-9}$
$SrSO_4$	1.1×10^{-1}	6.0×10^{-4}	$[Sr]\times[SO_4]=3.6\times10^{-7}$
TlBr	4.8×10^{-1}	1.7×10^{-3}	$[Tl]\times[Br]=2.9\times10^{-6}$
TlCNS	3.2	1.2×10^{-2}	$[Tl]\times[CNS]=1.4\times10^{-4}$
TlCl	3.4	1.4×10^{-2}	$[Tl]\times[Cl]=2.0\times10^{-4}$
TlI	6.4×10^{-2}	1.9×10^{-4}	$[Tl]\times[I]=3.6\times10^{-8}$
$Zn(OH)_2$	.....	.....	$[Zn]\times[OH]^2=1.8\times10^{-14}$
ZnS	3.3×10^{-10}	3.5×10^{-12}	$[Zn]\times[S]=1.2\times10^{-23}$

The above table is prepared from many sources, and the values are based, in some cases, upon solubility determinations by methods which are now considered inaccurate. The table gives a good idea, however, of the relative order of magnitude. For copper sulfide, the table states that 8.8×10^{-21} gms. dissolve in 1 liter of water. Obviously, the experimental determination of such a small value is fraught with difficulty and the probable error is large. For most purposes such a value represents a negligible quantity and the statement is often made that copper sulfide is insoluble in water. It is

instructive, however, to compare the solubility products of the various sulfides and important methods of separation have been based upon such studies. Only two significant figures have been given in the table, although it is obvious that more would be justifiable in the case of the more soluble substances, while even the first figure is doubtful for the very insoluble substances. The values are affected to different degrees by changes in temperature and the presence of other substances in solution. A careful, critical study of all the experimental data would be necessary to give the proper number of significant figures and it would be necessary to give the exact temperature.

In computing the solubility products, the assumption has been made that the ionization is complete. Such an assumption is not permissible with a substance such as ferric hydroxide, and in such cases only the approximate value of the solubility product is given; the molar solubility and the grams per liter are not stated. In other cases the ionization is abnormal as noted.

Two examples will be given to illustrate the method of computing the molar solubility, S_m, and the solubility product, S_p. A saturated solution of silver iodide contains 3.0×10^{-6} gms. ($= 0.0030$ mg.) per liter. The molecular weight of silver iodide is 234.8. The saturated solution, therefore, contains $\frac{3.0 \times 10^{-6}}{235} = 1.3 \times 10^{-8}$ moles. At this dilution the dissolved silver iodide can be assumed to be completely ionized:

$$AgI \rightleftarrows Ag^+ + I^-,$$

and since 1 mole of silver iodide furnishes 1 mole of silver ions and 1 mole of iodine ions, it is evident that the solubility product, S_p, is for $[Ag] \times [I] = [1.3 \times 10^{-8}] \times [1.3 \times 10^{-8}] = 1.7 \times 10^{-16} = S_p$.

A saturated solution of silver phosphate contains 6.5×10^{-3} gms. ($= 6.5$ mgs.) per liter. The substance is much more soluble in water than silver iodide, but its solubility product is smaller. The molecular weight of silver phosphate is 418.7. The saturated solution, therefore, contains $\frac{6.5 \times 10^{-3}}{419} = 1.6 \times 10^{-5}$ moles of silver phosphate which can be assumed to be completely ionized:

$$Ag_3PO_4 \rightleftarrows 3\,Ag^+ + PO_4^{---},$$

1 mole of silver phosphate yielding 3 moles of silver * and 1 mole of phosphate ions. The solubility product is

$$[Ag]^3 \times [PO_4] = [3 \times 1.6 \times 10^{-5}]^3 \times [1.6 \times 10^{-5}] = 1.8 \times 10^{-18} = S_p.$$

* If x moles of Ag_3PO_4 dissolve in a liter of water and the Ag_3PO_4 is completely ionized, the concentration of the Ag^+ is $3x$ and that of the PO^{---} is x when the con-

Complex Ions

Silver chloride is slightly soluble in water; 1 liter dissolves about 1.5 mgs. It dissolves very readily in dilute ammonia. The following reaction takes place:

$$AgCl + 2\,NH_3 \rightleftarrows Ag(NH_3)_2Cl.$$

A study of the properties of this new substance shows that it dissociates in aqueous solution chiefly in this way:

$$Ag(NH_3)_2Cl \rightleftarrows [Ag(NH_3)_2]^+ + Cl^-.$$

The ionic changes involved in the last two equations may be expressed thus:

$$AgCl \rightleftarrows Ag^+ + Cl^- \quad Ag^+ + 2\,NH_3 \rightleftarrows [Ag(NH_3)_2]^+$$

and, in accordance with the law of mass-action, the greater the concentration of the ammonia, the greater the extent to which the reaction takes place in the direction left to right. In a normal solution of ammonia, the ratio of the concentration of the $[Ag(NH_3)_2]^+$ ion to that of the simple Ag^+ ion is about $10^7 : 1$. The $[Ag(NH_3)_2]^+$ ion differs from the simple Ag^- ion in much the same manner as the ClO^-, ClO_2^-, or ClO_3^- ion differs from the simple Cl^- ion. It is called a *complex* cation.

When potassium cyanide is added to silver nitrate solution a white precipitate of silver cyanide is formed:

$$KCN + AgNO_3 = KNO_3 + AgCN,$$

---

centration is expressed in *moles per liter*. If the concentration is expressed in *equivalents per liter* (i.e., in terms of *normal* solutions), the x moles of Ag_3PO_4 furnish $3x$ equivalents of Ag_3PO_4 which ionize into $3x$ equivalents of Ag^+ and $3x$ equivalents of PO_4^{---}. The mass action law expression $\frac{[Ag]^3 \times [PO_4]}{[Ag_3PO_4]} = k$ holds for any method of expressing concentrations but it is, on the whole, simplest and best to express solubility products in *moles per liter*, and $[Ag]^3 \times [PO_4] = 27x^4$ in a saturated solution of silver phosphate containing x molecules of dissolved silver phosphate completely ionized. From the solubility product, the quantity of dissolved substance can be calculated. As one of the more complicated cases, let us consider lead phosphate. The solubility product, $[Pb]^3 \times [PO_4]^2$, is 1.5×10^{-32}. If x moles of $Pb_3(PO_4)_2$ dissolve in a liter of water and the salt is completely ionized, the solution will contain $3x$ moles of Pb^{++} and $2x$ moles of PO_4^{---} and

$$[Pb]^3 \times [PO_4]^2 = [3x]^3 \times [2x]^2 = 1.5 \times 10^{-32}$$

or,

$$108x^5 = 1.5 \times 10^{-32} = 0.015 \times 10^{-30}.$$

Then, with the aid of logarithms, it is easy to solve for x.

In applying the solubility product principle it is often necessary to remember that hydrolysis often takes place when the salt dissolves in water. In such cases the above methods of computation should be modified.

but if an excess of potassium cyanide is used the precipitate dissolves

$$AgCN + KCN = KAg(CN)_2.$$

In this case the ionic changes may be expressed as follows:

$$Ag^+ + CN^- \rightleftarrows AgCN,$$
$$AgCN + CN^- \rightleftarrows [Ag(CN)_2]^-$$

and the silver has become a part of the anion. In this case the value of the ratio of complex ion to simple ion is even larger than in the case of the silver ammonia cation.

Similarly, when insoluble ferrous cyanide is treated with an excess of potassium cyanide, it dissolves, forming potassium ferrocyanide,

$$Fe(CN)_2 + 4\,KCN = K_4[Fe(CN)_6].$$

This salt gives none of the ordinary reactions of ferrous ions. The iron forms an integral part of the complex ferrocyanide ion which has its own characteristic reactions, and during electrolysis always migrates toward the anode:

$$K_4[Fe(CN)_6] \rightleftarrows 4\,K^+ + [Fe(CN)_6]^{----}.$$

It is, in fact, quite common to find that simple salts, particularly in concentrated solutions, are capable of forming such complex compounds. The simple ions can unite with neutral molecules, or with ions of opposite charge, to form complex ions. If a simple ion adds to itself a neutral molecule, such as H_2O, H_2O_2, NH_3 or organic radicals, then neither the original valence nor the electric charge is changed. Thus the trivalent cobalt ion is capable of forming a deep red ion with 6 molecules of ammonia and this complex ion has a trivalent charge like that of the original simple ion.

$$Co^{+++} + 6\,NH_3 \rightleftarrows [Co(NH_3)_6]^{+++}.$$

If, in such a complex ion, one or more of the ammonia groups is replaced by a negative univalent ion, the valence of the complex ion is reduced one for each atom of negative ion thus entering into the complex

$$[Co(NH_3)_6]^{+++};\ [Co(NH_3)_5 \cdot NO_2]^{++};\ \left[Co\begin{matrix}(NO_2)_2\\(NH_3)_4\end{matrix}\right]^{+};\ \left[Co\begin{matrix}(NO_2)_3\\(NH_3)_3\end{matrix}\right].$$

In the presence of potassium cyanide, the trivalent cobalt ion unites with six CN^- ions to form a complex which has, in accordance with the above rule, a triple negative charge. *The valence or electric character of a complex ion is the algebraic sum of the valencies or electric charges of the constituents.*

As already indicated, the stability of these complex ions varies.

When the complex is very stable the common reactions of the constituents are not shown.

Besides these complex ions certain double salts are known. Thus potassium and aluminium sulfates crystallize together, forming an alum, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24\,H_2O$. When this salt is dissolved in water, the solution shows all the reactions for potassium, aluminium and sulfate ions, and there is little evidence of the formation of a complex ion. To determine, in a given case, whether a substance is a double salt or a complex salt, it is customary merely to see whether the characteristic reactions of the simple ions are shown. A salt exists which has the symbol $KCr(C_2O_4)_2 \cdot 5\,H_2O$. An aqueous solution of this salt readily shows the reactions for the potassium ions, but reacts sluggishly when tested for chromium cations or for oxalate anions. Evidently the chromium and the oxalate have united to form a complex anion with a negative valence of one, but this complex is not as stable as some of the others that have been mentioned. It is probable that there is no sharp distinction between the double salts and the complex salts and probably the double salts are most logically to be classed as complex salts of which the complex ion is not very stable. As a general rule, those complex salts which are composed of neutral salts of strong acids yield complex anions which are largely dissociated into simple ions in dilute solution. On the other hand, complex ions composed of positive ions and anions of weak acids are usually very stable.

Reactions of the Ions

As already indicated, most of the reactions used in qualitative analysis involve reactions between ions. We have seen that, in principle, all reactions are reversible and have learned to understand some of the laws which govern these reversible reactions. In analytical chemistry, it is necessary for the most part to employ reactions which take place almost completely in the desired direction. Unless a reaction can be made to go nearly to completion in a given direction, it is of little value either as a sensitive test or for furnishing a method of separation. The useful reactions of qualitative analysis, namely those which apparently go to completion, may be brought into four classes:

(1) Reactions in which a gas is formed
(2) Reactions in which a precipitate is formed.
(3) Reactions in which a non-ionized substance is formed.
(4) Reactions of oxidation and reduction.

When a gas is formed as a result of a chemical reaction and the gas escapes, the reaction will go to completion. Most gases can be boiled out of solution and thus all reactions of this type can be made to go to completion. The reaction can be stopped by preventing the escape of the gas; this shows that the reaction is inherently a reversible one.

Whenever a substance which has a very small solubility product is formed by means of a chemical reaction, the greater part of the substance will leave the solution in the form of a precipitate and the reaction will go practically to completion. The table on page 21 shows that the saturated solution of silver chloride contains only about one hundred-thousandth of a mole (= 0.01 millimole) of solid salt per liter. The table also shows that when the product obtained by multiplying the concentration of the silver ions by the product of the concentration of the chloride ions in any aqueous solution is equal to 1.2×10^{-10} the solution is saturated with silver chloride. By adding an excess of chloride ions to a solution containing silver ions, it is possible, therefore, to precipitate nearly all of the silver. It is evident that it will take less silver ions to give the solubility product when an excess of chloride ions is used than is necessary when pure silver chloride is dissolved in water.

The precipitated silver chloride will dissolve completely in potassium cyanide, because the silver ion forms with the cyanide ion a complex which is ionized to such a slight extent that the solubility product of silver chloride is no longer reached, even although all the chlorine is present in the ionic condition.

The formation of a non-ionized substance also causes a reaction to go to completion. The table on page 10 shows the ionization values of a few common substances. This table may be used exactly like that of the solubility products to enable one to predict whether a reaction is likely to go in a given direction. The equilibrium between water and its ions H^+ and OH^- has been discussed on page 6. The same reasoning may be applied to the equilibrium between any other slightly ionized substance and its ions; whenever the ions are added separately to a solution, some of the non-ionized substance is at once formed. Thus when any acid is added to the solution of a sulfide a reaction takes place, partly because the hydrogen sulfide is a very weak electrolyte and partly because the substance is a gas. Similarly calcium phosphate dissolves in hydrochloric acid because more PO_4^{---} ions are formed from dissolved calcium phosphate than are formed from $H_2PO_4^-$ ions in the presence of an excess of H^+ ions from the hydrochloric acid; the reaction takes place because of the formation of a non-ionized substance.

Finally, many reactions of oxidation and reduction take place nearly to absolute completion, although all these reactions can be shown to be inherently of a reversible type. To understand such equilibria, however, it is necessary to discuss oxidation and reduction at greater length.

Oxidation and Reduction

The term *oxidation*, in its narrowest sense, signifies the taking up of oxygen by an element or compound. Thus ferrous oxide, on being heated in the air, is converted into ferric oxide and the reaction is called an oxidation. Since, however, ferric chloride bears the same relation to ferrous chloride that ferric oxide bears to ferrous oxide, it is customary to call the change of ferrous chloride into ferric chloride an oxidation, although it is not necessary to think that oxygen takes part in the reaction at all. This is an interesting example of a word in common use which has come to mean a great deal more than it originally meant. Indeed, chemists have departed so far from the original meaning of *oxidation* that sometimes the word seems inappropriate, and the use of another word, such as *adduction*, has been suggested. Reduction is the exact opposite to oxidation, and whenever one substance is oxidized some other substance is reduced. Hydrogen was formerly considered to be the typical reducing agent, so that the definition for oxidation used to read something like this: Oxidation is the addition of oxygen (or its equivalent) to an element or compound or the taking away of hydrogen (or its equivalent).

The reaction between ferrous chloride and chlorine:

$$2\,FeCl_2 + Cl_2 = 2\,FeCl_3,$$

expressed in terms of the ionic theory becomes,

$$2\,Fe^{++} + Cl_2 = 2\,Fe^{+++} + 2\,Cl^-.$$

In other words, the *diferrion* has been converted to *triferrion* and the neutral chlorine molecule has become changed to negatively charged chloride ions. In all other reactions in which a ferrous salt is oxidized, the valence of the iron is increased one, and the modern conception of oxidation and reduction is summed up very simply as follows:

Oxidation is the increase in the valence of an element or radical in the positive direction; reduction is the increase in the valence of an element or radical in the negative direction. Oxidation involves the assumption of positive charges or the loss of negative charges and reduction involves the loss of positive charges or the assumption of negative charges.

According to the electronic conception of the constitution of matter, the atom of an element consists of positively charged corpuscles and

negatively charged corpuscles or electrons. The mass associated with the positive electricity is much larger than the mass associated with the equal charge of negative electricity. The number of positive and negative electrons which make up the atom is probably a very small multiple of the atomic weight of the element. The mass associated with a unit negative charge is so small that it may easily be lost, but only under conditions such that it is accepted by some other atom. The originally neutral atom which loses the electron thus becomes positively charged and the atom which accepts the negatively charged electron becomes negatively charged, and a tube of force holds the two elements together in a so-called chemical compound. In the light of the electron theory, therefore, an element is oxidized when it loses an electron and an element is reduced when it receives an electron. This is the simplest, and at the same time most comprehensive, theory of oxidation that has ever been suggested.

Oxidation, according to this conception, is essentially an electric phenomenon. This theory suggests the thought that it ought to be possible to accomplish oxidation and reduction simply by means of electric energy. As a matter of fact probably every oxidation and reduction can be brought about in the electrolytic cell if the proper conditions be maintained. Using the conventional symbol $\oplus$ to designate a unit charge of positive electricity and $\ominus$ to designate a unit charge of negative electricity, but bearing in mind that the negative electricity is alone transferred and that the only way an element can gain in positive charge is by losing one or more negative electrons, we may express oxidations in the electrolytic cell as follows:

$$Fe^{++} + \oplus \rightarrow Fe^{+++}, \quad \text{or} \quad Fe^{++} - \ominus \rightarrow Fe^{+++}.$$

Such oxidations take place at the electrode called the anode. Conversely, at the cathode, ferric salts can be reduced to the ferrous condition:

$$Fe^{+++} + \ominus \rightarrow Fe^{++}.$$

Not only may all oxidations and reductions be accomplished by the electric current, but, vice versa, an electric current may be produced by a proper arrangement of the components of any reaction of oxidation and reduction. Thus some ferric chloride and sodium chloride solution in a small beaker may be connected with a second beaker containing sodium chloride by means of a U-tube filled with dilute salt solution. If a platinum electrode is placed in each beaker and the terminals are connected with a sensitive voltmeter, no current will pass through the wire. On pouring some hydrogen sulfide water into the beaker containing sodium chloride, a decided deflec-

tion of the voltmeter needle is at once observed, showing the passage of electricity. The negative current enters the voltmeter from the solution containing the hydrogen sulfide and passes on to the ferric chloride solution and back, through the *salt-bridge*, to the hydrogen sulfide solution. The chemical reaction that takes place is,

$$2\,Fe^{+++} + S^{--} \rightarrow 2\,Fe^{++} + S.$$

The electric current is produced as a result of the oxidation of the sulfide ions and reduction of the ferric ions.

Oxidation and reduction reactions are inherently reversible reactions, like all other chemical reactions, and are effected by the concentrations of the reacting substances. Thus, in the above experiment the intensity of the electric current can be greatly increased by using a soluble sulfide instead of hydrogen sulfide, the former being more largely dissociated and yielding a larger concentration of sulfide ions. Or, by adding a fluoride to the solution of ferric chloride, a fairly stable complex ion, $[FeF_6]^{---}$, is formed and the current slackens, owing to the decreased concentration of the ferric ions.

Some of the more important oxidizing agents used in analytical chemistry are the *halogens, nitric acid, potassium permanganate, potassium dichromate* and *hydrogen peroxide.*

Important reducing agents are *metals, sulfurous acid, hydrogen sulfide, stannous chloride* and *hydriodic acid.*

The oxidizing action of halogens depends upon the conversion of the neutral halogen into halogen anions.

The oxidizing action of halogen upon ferrous ions results in the formation of ferric ions and of halide ions:

$$2\,Fe^{++} + Cl_2 \rightarrow 2\,Fe^{+++} + 2\,Cl^-,$$

or

$$2\,FeCl_2 + Cl_2 = 2\,FeCl_3.$$

The action of halogen upon hydrogen sulfide is interesting. First of all, the sulfide ion is oxidized to free sulfur,

$$H_2S + Br_2 \rightarrow 2\,HBr + S,$$

but, if the bromine is fairly concentrated, the reaction may go farther and the sulfur be converted into sulfuric acid, the whole reaction being

$$H_2S + 4\,Br_2 + 4\,H_2O = H_2SO_4 + 8\,HBr.$$

It will be noticed that it is very easy to balance equations of oxidation and reduction by noticing the change in valence. In this last equation sulfur goes from a negative valence of two to a positive valence of six, making an algebraic change of eight, which corresponds to the loss of eight electrons by the sulfur atom.

The oxidizing action of nitric acid depends upon the reduction of the nitrogen. The extent of the reduction depends upon the concentration of the nitric acid and the nature of the substance oxidized. The more concentrated the nitric acid, the less it is reduced; the more concentrated the reducing agent and the stronger its reducing power the greater the reduction of the nitric acid. Nitric oxide, NO, is commonly formed, but often other products such as nitrogen peroxide, nitrous oxide, nitrogen and even ammonia are produced.

In nitric acid, the nitrogen atom has five positive electric charges residing upon it. When it is reduced to nitric oxide, NO, it has only two positive charges, the nitrogen having accepted three electrons. The reaction between a ferrous salt and nitric acid is,

$$3\,Fe^{++} + NO_3^- + 4\,H^+ \rightarrow 3\,Fe^{+++} + NO + 2\,H_2O,$$

or

$$6\,FeSO_4 + 2\,HNO_3 + 3\,H_2SO_4 = 3\,Fe_2(SO_4)_3 + 2\,NO + 4\,H_2O.$$

The reaction is doubled in the last instance simply to get an even number of molecules of $Fe_2(SO_4)_3$. The addition of sulfuric acid is unnecessary, as the nitric acid can also act as an acid, in which case a mixture of ferric sulfate and nitrate is formed:

$$3\,FeSO_4 + 4\,HNO_3 = Fe_2(SO_4)_3 + Fe(NO_3)_3 + NO + 2\,H_2O.$$

The action of nitric acid on a sulfide is interesting. If the nitric acid solution is cold and dilute (0.3 N) there is hardly any oxidation of the sulfur:

$$MnS + 2\,HNO_3 = Mn(NO_3)_2 + H_2S\uparrow.$$

If the nitric acid is more concentrated (e.g., 2 N) and the solution is heated, the sulfide is changed to nitrate and free sulfur is formed. Thus for the reaction between copper sulfide and hot nitric acid, each atom of sulfur loses two electrons and, in accomplishing the oxidation, an atom of nitrogen gains three electrons. The reaction may be expressed thus:

$$3\,CuS + 8\,HNO_3 = 3\,Cu(NO_3)_2 + 4\,H_2O + 3\,S + 2\,NO,$$

or

$$3\,CuS + 8\,H^+ + 2\,NO_3^- \rightarrow 3\,Cu^{++} + 4\,H_2O + 3\,S + 2\,NO.$$

If the nitric acid is very concentrated, the greater part of it is reduced only to NO_2 and the sulfur is oxidized to sulfuric acid. The reaction may then be written:

$$CuS + 8\,HNO_3 = CuSO_4 + 8\,NO_2 + 4\,H_2O.$$

The oxidizing action of permanganate depends upon the readiness with which the manganese is converted into a manganese com-

pound of lower valence. In the permanganate anion, MnO_4^-, the manganese has a positive valence of seven. Ordinarily, in acid solution, the permanganate is reduced to bivalent manganese cation, corresponding to a loss of five positive charges, or acceptance of five electrons:

$$MnO_4^- + 5\,Fe^{++} + 8\,H^+ = Mn^{++} + 5\,Fe^{+++} + 4\,H_2O;$$

$$2\,MnO_4^- + 5\,H_2S + 6\,H^+ = 2Mn^{++} + 5\,S + 8\,H_2O;$$

$$2\,MnO_4^- + 5\,Sn^{++} + 16\,H^+ = 2\,Mn^{++} + 5\,Sn^{++++} + 8\,H_2O;$$

$$2\,MnO_4^- + 10\,HI + 6\,H^+ = 2\,Mn^{++} + 5\,I_2 + 8\,H_2O.$$

The oxidizing action of a chromate or dichromate ordinarily depends upon the formation of trivalent chromic ions. In the chromate and dichromate ions the chromium atom has a positive valence of six, so that for each atom of chromium the reduction corresponds to a loss of three positive charges, or gain of three electrons. Potassium chromate in acid solution is in equilibrium with the dichromate:

$$2\,CrO_4^{--} + 2\,H^+ \rightarrow 2\,HCrO_4^- \rightarrow H_2O + Cr_2O_7^{--}.$$

In balancing equations, therefore, it makes little difference whether we start with the chromate or dichromate, except with respect to the quantity of acid required:

$$Cr_2O_7^{--} + 6\,Fe^{++} + 14\,H^+ \rightarrow 2\,Cr^{+++} + 6\,Fe^{+++} + 7\,H_2O;$$

$$Cr_2O_7^{--} + 3\,S^{--} + 14\,H^+ \rightarrow 2\,Cr^{+++} + 3\,S + 7\,H_2O;$$

$$Cr_2O_7^{--} + 3\,Sn^{++} + 14\,H^+ \rightarrow 2\,Cr^{+++} + 3\,Sn^{++++} + 7\,H_2O;$$

$$Cr_2O_7^{--} + 6\,I^- + 14\,H^+ \rightarrow 2\,Cr^{+++} + 3\,I_2 + 7\,H_2O.$$

Hydrogen peroxide acts both as an oxidizing agent and as a reducing agent. It oxidizes ferrous chloride to ferric chloride and it is capable of reducing permanganate to manganous salt. This anomalous behavior has been the cause of considerable discussion in the literature. It is unnecessary to go into the details of such a discussion, but a simple explanation of this behavior will be suggested. In all the other compounds of hydrogen and oxygen that we shall study, hydrogen has a positive valence of one and oxygen a negative valence of two. With hydrogen peroxide, also, it is best to assume that the hydrogen has its normal valence corresponding to one positive charge. Two structural formulas are at once suggested for hydrogen peroxide,

$$\begin{matrix} H \searrow \\ H \nearrow \end{matrix} O \rightleftarrows O \quad \text{or} \quad \begin{matrix} H \rightarrow O \\ \\ H \rightarrow O \end{matrix} \uparrow .$$

Each of these formulas gives to one atom of oxygen its normal negative charge of two units of electricity and each gives to one atom of oxygen an equal number of positive and negative charges. It is unnecessary, therefore, to attempt to decide which of these formulas is the more appropriate.

The characteristic behavior of hydrogen peroxide may be traced to the presence of the atom of oxygen which has an equal number of positive and negative charges. In alkaline solution, hydrogen peroxide decomposes spontaneously and oxygen is evolved. This spontaneous decomposition, with the formation of neutral oxygen, is easy to understand on the basis of the assumption that the original molecule already contains the atom of oxygen in a very unstable condition of neutrality.

The oxidizing power of hydrogen peroxide is due to this atom of oxygen. In acid solutions ferrous iron is converted by it to the ferric condition. The peculiar atom of oxygen loses its positive charge and receives in its place a negative charge; the total change corresponding to the acceptance of two electrons:

$$2\,Fe^{++} + H_2O_2 + 2\,H^+ \rightarrow 2\,Fe^{+++} + 2\,H_2O.$$

The reducing power of hydrogen peroxide also depends upon the presence of this atom of oxygen. When in contact with a powerful oxidizing agent, such as permanganate or another peroxide, a reaction takes place and oxygen gas is evolved. It has always been assumed, since the classic experiments of Schönbein, that half of the evolved oxygen comes from the oxidizer and half from the hydrogen peroxide. It is simplest to assume, therefore, that the oxygen is momentarily changed to an atom with two positive charges which at once unites with negatively charged oxygen in the oxidizer; or, this oxygen in the hydrogen peroxide may unite with similarly charged oxygen in another peroxide.

$$2\,MnO_4^- + 5\,H_2O_2 + 6\,H^+ \rightarrow 2\,Mn^{++} + 8\,H_2O + 5\,O_2;$$

$$MnO_2 + H_2O_2 + 2\,H^+ \rightarrow Mn^{++} + 2\,H_2O + O_2;$$

$$Co_2O_3 + H_2O_2 + 4\,H^+ \rightarrow 2\,Co^{++} + 3\,H_2O + O_2.$$

The characteristic action of the more important oxidizing agents has now been considered briefly and it remains to describe the characteristic behavior of the important reducing agents. Since every oxidation involves a simultaneous reduction, all of the above reactions can be used to illustrate reduction as well as oxidation.

The reducing action of hydrogen and of metals depends upon the conversion of the neutral hydrogen * or metal into positively charged cations. Such a reduction may take place in acid, alkaline or neutral solution.

(*a*) In acid solution, by the employment of zinc, etc.:

$$Zn + H_2SO_4 = ZnSO_4 + H_2\uparrow$$

or

$$Zn + 2\,H^+ \rightarrow Zn^{++} + H_2\uparrow.$$

This reaction in itself represents both an oxidation and a reduction, inasmuch as the metallic zinc, which is electrically neutral, becomes changed into zinc with two positive charges and, on the other hand, the hydrogen in sulfuric acid has lost two charges and become electrically neutral hydrogen.

If there is some other ion present in the solution which is easier to reduce than the hydrogen ion, it is possible that no hydrogen will be evolved. Thus zinc can be amalgamated so that it will not react with acid and yet will reduce ferric ions to the ferrous condition:

$$2\,Fe^{+++} + Zn = Zn^{++} + 2\,Fe^{++}.$$

By the action of zinc and very dilute sulfuric acid, it is easy to transform silver chloride into metallic silver:

$$2\,Ag^+ + Zn \rightarrow Zn^{++} + 2\,Ag,$$

or an arsenite into arsine:

$$AsO_3^{---} + 3\,Zn + 9\,H^+ \rightarrow 3\,Zn^{++} + 3\,H_2O + AsH_3.$$

The result of this last equation is the oxidation of zinc from the metallic condition to the bivalent state and the reduction of the arsenic which is given three negative charges in place of the three positive charges

* Formerly, before the theory of oxidation and reduction potentials was known, it was customary to refer many of the reductions taking place in aqueous solution to the action of *nascent hydrogen*. Nascent hydrogen was the name given to hydrogen in the state in which it exists at the moment it is set free from a compound.

In the older nomenclature, the reducing action of sulfurous acid was attributed perhaps to the "affinity" that this substance had for oxygen. If the oxygen was obtained from water, then the hydrogen at the moment it was set free was assumed to be capable of causing reductions which hydrogen could not ordinarily accomplish. Similarly when zinc reacts with dilute acid, hydrogen is evolved and because zinc in the presence of dilute acid will accomplish reductions which hydrogen in its normal condition was incapable of effecting, it was customary to consider the action of zinc and acid to *nascent hydrogen*.

The reducing power of an element, however, is determined by its specific reduction potential (cf. p. 37). The higher the element stands in the electromotive series, the easier it is oxidized and the greater is its power as a reducing agent. In most cases, to-day, the use of the term *nascent hydrogen* is unnecessary.

it has in AsO_3^{---}. Thus each As atom loses six charges of electricity and each Zn atom gains two, so that it takes three Zn atoms to reduce one AsO_3^{---} anion.

(*b*) In alkaline solution, by means of zinc, aluminium, sodium amalgam, or by Devarda's Alloy (Cu = 50, Zn = 5, Al = 45).

$$Zn + 2\,OH^- \rightarrow ZnO_2^{--} + H_2\uparrow$$

$$2\,Al + 2\,OH^- + 2\,H_2O \rightarrow 2\,AlO_2^- + 3\,H_2\uparrow.$$

In the case of Devarda's Alloy, the reaction is completed much more quickly than by the use of either zinc or aluminium alone. Nitrates and chlorates may be reduced in a few minutes by means of Devarda's Alloy and a few drops of sodium hydroxide; the reaction also takes place in neutral solution, but it takes considerably longer:

$$NO_3^- + 4\,Zn + 7\,OH^- \rightarrow 4\,ZnO_2^{--} + 2\,H_2O + NH_3$$

$$ClO_3^- + 3\,Zn + 6\,OH^- \rightarrow 3\,ZnO_2^{--} + 3\,H_2O + Cl^-.$$

In the nitrate ion nitrogen has a positive valence of five; in ammonia it has a negative valence of three. By the reduction with zinc, therefore, the nitrogen loses eight positive charges, or accepts eight electrons. At the same time the zinc loses two electrons, forming, in a neutral or alkaline solution, the zincate anion. Thus one atom of nitrogen in the nitrate ion requires four atoms of zinc to convert it into ammonia.

Similarly, the chlorine atom in the *chlorate ion* has a positive valence of five and is reduced to a negative valence of one by the reaction with zinc in neutral or alkaline solution. Thus one chlorate ion reacts with three atoms of zinc. Inspection of the above equilibrium expressions shows that one could predict that the reactions would take place best in alkaline solution in accordance with the mass-action law.

Reduction by means of sulfurous acid takes place in moderately acid solution and depends upon the fact that sulfur is more stable when it has six positive charges, as in sulfuric acid, than when it has only four as in sulfurous acid. Ferric salts are readily reduced by this reagent, and since the iron loses only one valence while the sulfur gains two, it is evident that one molecule of sulfur dioxide (the anhydride of sulfurous acid) will reduce two atoms of iron in a ferric salt:

$$Fe_2(SO_4)_3 + 2\,H_2O + SO_2 = 2\,H_2SO_4 + 2\,FeSO_4,$$

or

$$2\,Fe^{+++} + SO_3^{--} + H_2O \rightarrow 2\,Fe^{++} + SO_4^{--} + 2\,H^+.$$

In a similar manner, the arsenate ion and many other substances are reduced very readily by means of SO_2 or SO_3^{--}:

$$AsO_4^{---} + SO_3^{--} \rightarrow AsO_3^{---} + SO_4^{-}$$

An excess of aqueous sulfurous acid is added to the solution which is to be reduced; it is then heated to boiling; and the boiling is continued while a stream of carbonic acid gas is passed through the solution until the excess of sulfurous acid is driven off.

Reduction by means of hydrogen sulfide, in which the sulfur atom possesses two negative charges, depends upon its oxidation to free sulfur, which is electrically neutral. Thus two atoms of ferric iron are reduced to ferrous iron by one molecule of hydrogen sulfide and one molecule of potassium dichromate reacts with three molecules of hydrogen sulfide:

$$2\,Fe^{+++} + H_2S \rightarrow 2\,Fe^{++} + 2\,H^+ + S$$
$$Cr_2O_7^{--} + 3\,H_2S + 8\,H^+ \rightarrow 2\,Cr^{+++} + 3\,S + 7\,H_2O.$$

One objection to the use of hydrogen sulfide as a reducing agent is the difficulty involved in the subsequent removal of the precipitated sulfur by filtration. Moreover, hydrogen sulfide is used in qualitative analysis chiefly as a precipitant. If a solution contains an oxidizing agent (such as nitric acid, chloric acid, chromic acid, etc.), the sulfide ion will be oxidized and there will be separation of sulfur. Any sulfide obtained will be largely contaminated with sulfur, which renders the subsequent examination more difficult. If the solution contains no metal which is precipitated by hydrogen sulfide, but contains oxidizing agents, it will still cause separation of sulfur. One is often in doubt whether there is not some sulfide mixed with the sulfur, and is therefore obliged to examine the precipitate further, which is often unnecessary if the oxidizing agent is previously destroyed. Hydrogen sulfide reduces

Halogens:	$H_2S + Cl_2$	$= 2\,HCl + S;$
Nitric Acid:	$2\,HNO_3 + 3\,H_2S$	$= 4\,H_2O + 2\,NO + 3\,S;$
Chloric Acid:	$HClO_3 + 3\,H_2S$	$= 3\,H_2O + HCl + 3\,S;$
Ferric Salts:	$2\,FeCl_3 + H_2S$	$= 2\,HCl + 2\,FeCl_2 + S;$
Chromic Acid:	$2\,CrO_3 + 3\,H_2S + 6\,H^+$	$= 6\,H_2O + 2\,Cr^{+++} + 3\,S;$
Permanganic Acid:	$2\,HMnO_4 + 5\,H_2S + 4\,H^+$	$= 8\,H_2O + 2\,Mn^{++} + 5\,S;$

and many other substances.

Reduction with stannous chloride takes place usually in acid solutions. The reduction depends upon the fact that stannous ions are readily changed to stannic ions:

$$SnCl_2 + Cl_2 = SnCl_4,$$

or

$$Sn^{++} + Cl_2 = Sn^{++++} + 2\,Cl^-.$$

Ferric salts, chromates, permanganates, mercuric salts, and many others are reduced in this way:

$$2\,Fe^{+++} + Sn^{++} \rightarrow 2\,Fe^{++} + Sn^{++++};$$

$$2\,CrO_4^{--} + 3\,Sn^{++} + 16\,H^+ \rightarrow 2\,Cr^{+++} + 3\,Sn^{++++} + 8\,H_2O;$$

$$2\,HgCl_2 + Sn^{++} \rightarrow Sn^{++++} + Hg_2Cl_2 + 2\,Cl^-;$$

$$Hg_2Cl_2 + Sn^{++} \rightarrow Sn^{++++} + 2\,Hg + 2\,Cl^-.$$

Reduction with hydriodic acid depends upon the change of the iodine anion into free iodine. Most substances that are capable of being oxidized or reduced readily can be made to react with either hydriodic acid or with free iodine. It is easy to detect the presence of free iodine, and for this reason the iodometric reactions are extremely important in the study of analytical chemistry. To prevent the oxidizing effect of free iodine, an excess of potassium iodide is usually required, and means are often taken to remove the iodine as fast as it is formed; this is in accordance with the mass-action principle,

$$2\,MnO_4^- + 10\,I^- + 16\,H^+ \rightarrow 2\,Mn^{++} + 8\,H_2O + 5\,I_2;$$

$$Cr_2O_7^{--} + 6\,I^- + 14\,H^+ \rightarrow 2\,Cr^{+++} + 7\,H_2O + 3\,I_2;$$

$$2\,Fe^{+++} + 2\,I^- \rightarrow 2\,Fe^{++} + I_2.$$

Electromotive Series and Reduction Potentials

If a substance like sugar lies as a solid on the bottom of a beaker filled with water, the molecules of sugar tend to distribute themselves throughout the solution; in other words, the sugar dissolves. The tendency of the solid molecules to pass into solution may be regarded as the result of pressure and, in fact, it is customary to say that the solid substance possesses a *solution pressure*.

If sufficient solid is present, eventually, with the aid of diffusion, the liquid will reach a state of saturation. The liquid then contains an equal quantity of sugar in all its parts and, at the prevailing temperature, will not dissolve any more sugar. There must, therefore, be some force which acts in opposition to the solution pressure and prevents a saturated solution from dissolving any more of the solid substance. This force is the *osmotic pressure* which the dissolved molecules exert in the solution. In a saturated solution, the osmotic pressure, which is itself determined solely by the number of molecules of dissolved substance and the temperature, exactly balances the solution pressure of the solid substance. The process of dissolving a solid substance involves no electrical effects. This is also true when the dissolved substance is an ordinary electrolyte, because an equal number

of positive and negative ions is formed and there is no electric disturbance.

The metals themselves, though usually to a much less degree, also show a tendency to dissolve when placed in contact with water. In this case, however, an oxidation takes place, for, to the extent that it dissolves, the metal is converted into electrically charged ions. The tendency of the metal to dissolve is called its *electrolytic solution pressure.* Just as in the case of the sugar, the osmotic pressure of the dissolved ion acts against the solution pressure. The electrolytic solution pressure has a definite value which is characteristic of each metal.

If a metal such as zinc, which oxidizes fairly readily, is placed in a *saturated* solution of zinc sulfate, none of the metal dissolves. If it is placed in contact with a *dilute* solution of zinc sulfate, the solution pressure of the zinc is greater than the deposition pressure and some positively charged zinc ions pass into solution. Thereby, the metal itself acquires a negative charge and the solution a positive charge. As a result of the charge residing upon the zinc ions that have gone into solution, an electrostatic force is produced which seeks to force the ions back upon the metal. This electromotive force is added to the osmotic pressure of all the zinc ions in solution and it increases rapidly with the number of ions that dissolve from the metal. When the sum of the osmotic pressure plus the electromotive force is equal to the electrolytic solution pressure of the zinc the zinc stops dissolving.

When a less-readily oxidizable metal, such as copper, is placed in a copper sulfate solution the relations are reversed. In this case, except in extremely dilute solutions, the osmotic pressure is greater than the solution pressure and the metal does not dissolve; on the contrary, a few of the copper ions are discharged on the metal, giving to it a positive charge while the solution becomes negatively charged. Equilibrium is established as soon as a few of the ions have been thus deposited. The potential difference between the metal and its solution, or, as it may be called, the reduction potential of the metal, is said to be positive when the charge of the solution is positive; this is the case with the readily oxidizable metals such as magnesium, aluminium, zinc, iron, etc. On the other hand, the reduction potential of the metal is negative when it is difficultly oxidizable; this is the case with copper, silver, platinum and gold.

Simple contact of a metal with a solution of its ions usually results in a potential difference between the metal and the solution. Such a potential is determined by the relation that exists between the electrolytic solution pressure of the metal and the

osmotic pressure of the solution. Equilibrium is soon reached in most cases and the simple contact of a metal with a solution of its ions is not a permanent source of electricity. If, however, two metals of different potential are placed in contact with their respective solutions, then electric charges of different potentials result, and if the two metals are connected outside the liquids by a wire, an electric current flows from the higher potential to the lower. Since the original differences in potential between the solutions and the metals are constantly being reëstablished, a permanent current results. This is the principle of the Daniell cell, in which a normal solution of copper sulfate is separated by a porous partition from a normal solution of zinc sulfate. A zinc rod is placed in the zinc sulfate solution and a copper plate in the copper sulfate solution; the current flows through the wire from the copper to the zinc and through the solution from the zinc to the copper.

In the case of metals, *electrolytic solution tension* and *reduction potential* refer to the same property.

Nernst, who was the first to suggest the above explanation of the origin of the electromotive force on the basis of the relations of osmotic pressure, has worked out a formula for computing the potential difference which exists at the place of contact of a metal with a solution of its ions. If E denotes this potential in volts, R the gas constant expressed in volts × coulombs,* F the electrochemical equivalent or quantity of electricity borne by one equivalent weight in grams of the ions of any metal, n the valence of the ions, P the electrolytic solution pressure, p the osmotic pressure, and T the absolute temperature of the solution, the Nernst formula reads:

$$E = \frac{RT}{nF} \log_e \frac{P}{p}.$$

Substituting the numerical values for R (8.32) and F (96,500), dividing by 0.434 in order to use common logarithms, and assuming the ordinary room temperature to be 18° C. (= 291° absolute), the formula becomes:

$$E_{18°} = \frac{0.058}{n} \log \frac{P}{p} \text{ volts.}$$

Inasmuch as the osmotic pressure, p, depends solely upon the concentration of the solution and the temperature, the electromotive force resulting by the contact of a metal with its ions is shown by the formula to increase as the electrolytic solution pressure of the metal increases and to decrease as the concentration of the ions increases. Since multiplying a number by 10 simply raises its common logarithm

* Ergs or watt-seconds.

one whole unit, the formula also shows that increasing the concentration of the solution tenfold lowers the electromotive force in question about 0.06 volt when the ions are univalent, 0.03 volt when the ions are bivalent, and 0.02 volt when the ions are trivalent. Lowering the concentration until it is one-tenth of its original value raises the electromotive force nearly 0.06 volt in the case of univalent ions, 0.03 volt with bivalent ions, and 0.02 volt with trivalent ions. The electrolytic solution pressure is a measure of the readiness with which a metal can be converted into its ions; or, since the formation of the ions involves an oxidation, it determines the readiness with which the element undergoes oxidation. As already mentioned, the electromotive force that results can be appropriately called the *reduction potential.** It is also a measure of the force required to deposit a metal from solution by means of the electric current.

It is now easy to understand what happens when a metal is placed in a solution containing the ions of some other metal. It is a well-known fact that the immersion of a strip of iron in a solution of copper sulfate causes the deposition of metallic copper, while an equivalent quantity of iron dissolves as ferrous sulfate. The copper is reduced to the metallic condition by means of metallic iron and the latter is oxidized by means of cupric ions. This is because the electrolytic solution pressure of iron is so much greater than that of copper that a condition of equilibrium is not reached until practically all of the copper has been precipitated. The reduction potential of metallic iron against a molal solution of a ferrous salt is 0.43 volt and of metallic copper against a molal solution of cupric ions is about -0.34; the minus sign means merely that there is more tendency for copper ions to be deposited than for metallic copper to pass into solution. The greater the positive value of the reduction potential, the greater the electrolytic solution pressure. As the copper is deposited from the solution, its reduction potential gradually becomes larger, and as the iron passes into solution its reduction potential becomes smaller and smaller. The Nernst formula shows that the value for metallic copper against a tenth-molal solution of its ions will be raised to -0.31 volt and the value for iron against a solution of tenth-molal ferrous salt will

* In some respects it is more logical to call this the *oxidation* potential of the metal but physicists, as a rule, assign *negative* values to the oxidation potentials of the so-called *positive* elements which have high solution pressures.

The value of E in the Nernst formula represents the *actual reduction potential*, or reducing power, of a solution in contact with a solution of its ion. The formula shows how this *actual* voltage depends not only upon the solution tension of the element, but also upon the temperature, the valence of the ions, and the concentration of the solution.

be 0.46 volt. It is evident that equilibrium between the iron and the cupric solution will be reached only when the reduction potential of the iron is equal to the reduction potential of the copper; before this happens either the solution will become saturated with ferrous sulfate or all but an infinitesimal quantity of the copper will be precipitated.

It is possible to arrange all the metals in a series according to their electrolytic solution pressures. Such a series is called the *electromotive series* of the metals. It enables one to understand all the reactions in which a free metal is involved either as an initial or a final product. The entire chemical activity of the metals corresponds fairly closely with such an arrangement. The members at the top of the series are the most readily oxidizable; those following copper do not oxidize or rust when exposed to the air.

The electromotive series shows the relative value of the metals as reducing agents. The metals at the top of the series are the best reducing agents. Thus the alkalies are such good reducing agents that they will even decompose water at ordinary temperatures, reducing the positively charged hydrogen to the neutral condition.

It is important to remember, however, that it is not alone the electrolytic solution tension which determines the reduction potential. The concentration of the solution also comes into consideration. If the reduction potentials are all measured against equivalent concentrations, then the order of the metals arranged in the electromotive series will correspond exactly to the order of the metals when arranged according to the values of their electrolytic solution pressures.

ELECTROMOTIVE SERIES OF THE METALS.

Cæsium
Rubidium
Potassium
Sodium
Magnesium
Aluminium
Manganese
Zinc
Cadmium
Thallium
Iron
Cobalt
Nickel
Tin
Lead
Hydrogen
Antimony
Bismuth
Arsenic
Copper
Mercury
Silver
Palladium
Platinum
Gold

We are now able to understand why the alkali metals decompose water to form alkali ions and why the quantity of zinc ions formed under similar conditions is very small. The reduction potential of zinc against a molal solution of zinc ions is about 0.76 volt. Water, however, is ionized very slightly; the table on page 10 gives its ionization as 2×10^{-7} per cent. The reduction potential of hydrogen against such a very dilute solution of hydrogen is not 0.0, as given in the table, but it is nearer the zinc value. If the ionization of water were 10^{-26}, the value would be approximately that of zinc. According to the reduction potentials, therefore, we should expect zinc to decompose water with liberation of gaseous hydrogen. As a matter of fact zinc is oxidized somewhat by contact with water and the oxidizing agent is the hydrogen of

water; but the reaction does not take place to any extent. The primary products of the reactions are zinc ions and free hydrogen, but the escape of the hydrogen leaves free hydroxyl ions in solution and these are in equilibrium with the zinc ions. The table on page 22 gives the solubility product of zinc hydroxide as 1.8×10^{-14}. The reason the zinc does not decompose water, therefore, is because it is protected by the film of insoluble oxide or hydroxide which quickly forms upon it. On the other hand, when the hydrogen is present in the form of an acid, with the anion of which zinc forms a fairly soluble salt, the oxidation of the zinc ordinarily continues at the expense of hydrogen ions until all of the zinc is dissolved.*

We have seen that the Daniell cell † is obtained by taking advantage of a difference in reduction potentials, and it was stated on page 29 that a similar cell could be formed by taking advantage of any reaction of oxidation and reduction. All reactions of oxidation and reduction take place because of differences in reduction potentials. Just as the electromotive series of the metals helps one to predict whether a metal will act as a reducing agent or not, so a complete table of reduction potentials will help one to determine whether any given reaction of oxidation and reduction may be expected to take place in the desired direction. Such a table of reduction potentials is given on page 44. The table shows the values referred to molal solutions, the value of

* There is another important reason why zinc does not react with water. Hydrogen ions are discharged with different degrees of readiness by electrolysis when cathodes of different metals are used. It is easiest to discharge hydrogen when an electrode of unpolished platinum is used and more voltage is required with zinc and other metals. This so-called *over-voltage* is large enough in the case of zinc to permit the quantitative deposition of this metal by electrolysis of solutions containing acetic acid and sodium acetate. The values given on page 44 are based on the normal discharge of hydrogen and if the over-voltage of hydrogen toward zinc is considered, it brings the reduction potential of hydrogen higher in the series.

† In the well-known Daniell cell the zinc, which is in contact with zinc sulfate solution, is the negative electrode, and the copper, which is in contact with copper sulfate solution, is the positive electrode; zinc passes into solution at one electrode and copper is deposited at the other. Outside the cell, the positive-to-negative direction is from copper to zinc, but inside the cell it is from zinc to copper. In measuring the single electrode-potentials of such a cell, physicists assign a negative value to the potential of the element which dissolves and a positive value to the element which is deposited. In the Daniell cell, however it seems rational to assign a positive value to the electromotive force which measures the tendency of zinc to form zinc ions, and a negative value to the tendency of copper to form copper ions. In this book, therefore, the positive values will be assigned to the elements with high solution tension and, to avoid confusion, the voltages will be called *reduction potentials*. The oxidation potentials will have the same numerical values but with opposite sign. Cf. A. A. NOYES, *Qualitative Chemical Analysis*, pp. 81 and 181 (1920).

normal hydrogen ions in the normal hydrogen electrode being taken as 0. The positive value of the electromotive force shows that the oxidation takes place very readily, the unchanged substance assuming a negative charge; or, in other words, if a cell is constructed with the normal hydrogen electrode, the direction of the current (positive to negative) *in the solution* is toward the hydrogen electrode when the element has a positive potential. The first column in the table gives the original state of the element or ion, the second column shows the change in charge that this element or ion undergoes, the third column the oxidized condition and the fourth column the reduction potential.

The electromotive force of any reaction of oxidation and reduction is determined by the difference in the reduction potentials. Thus in the Daniell cell using molal solutions of copper sulfate and zinc sulfate, the electromotive force of the entire cell is the difference between the reduction potentials of copper (-0.34 volt) and zinc ($+0.76$) = 1.10 volts.

The table of reduction potentials will help to explain many of the reactions used in analytical chemistry. All the metals above hydrogen will replace the hydrogen of dilute acids; those below hydrogen will not do so as a rule.

The oxidation of copper to cupric ions corresponds to a potential of -0.34 volt and this explains why copper is not dissolved by hydrochloric acid. Any oxidizing agent capable of oxidizing copper from the metallic to the ionic condition will at once form cupric ions because the oxidation of cuprous to cupric ions corresponds to only -0.17 volt, and that of copper to cuprous ions is -0.51 volt. In the presence of some agent whose reduction potential is low in the series, copper will dissolve. Such an oxidizing agent is the ferric ion, for the table shows that the oxidation potential of ferrous ions to ferric ions is -0.75 volt; just as cupric ions will oxidize metallic iron to the ferrous condition so will ferric chloride oxidize metallic copper to the cupric condition:

$$2\,Fe^{+++} + Cu \rightarrow Cu^{++} + 2\,Fe^{++}.$$

The table shows where interference is to be expected. Metallic aluminium will precipitate iron from a solution of a ferrous salt. It will not precipitate iron if an acid is present because, as the table shows, iron will itself liberate hydrogen gas from hydrogen ions; on the other hand, from the oxidation potential of ferrous to ferric ions, it is evident that metallic aluminium will reduce a ferric solution before acting upon the hydrogen ions of the acid. It also shows that metallic aluminium will precipitate copper completely even in the presence of acid.

REDUCTION POTENTIALS IN MOLAL SOLUTIONS *

Original State.	Increase in Valence.	Oxidized State.	E.m.f. in volts.
Li°	1	Li^+	+3.03
K°	1	K^+	+2.93
Na°	1	Na^+	+2.72
Ba°	2	Ba^{++}	+2.8
Sr°	2	Sr^{++}	+2.7
Ca°	2	Ca^{++}	+2.6
Mg°	2	Mg^{++}	+1.5
Al°	3	Al^{+++}	+1.3
Mn°	2	Mn^{++}	+1.1
Zn°	2	Zn^{++}	+0.76
S^{--}	2	S°	+0.55
Fe°	2	Fe^{++}	+0.43
Cd°	2	Cd^{++}	+0.40
$Pb^\circ + SO_4^{--}$	2	$PbSO_4$ solid	+0.34
Co°	2	Co^{++}	+0.23
Ni°	2	Ni^{++}	+0.22
$Cu^\circ + 2OH^-$	2	$Cu(OH)_2$ solid	+0.21
Pb°	2	Pb^{++}	+0.12
Sn°	2	Sn^{++}	+0.10
Fe°	3	Fe^{+++}	+0.04
H_2 gas	2	$2H^+$	±0.00
Sb°	3	Sb^{+++}	−0.1†
Sn^{++}	2	Sn^{++++}	−0.14†
Cu^+	1	Cu^{++}	−0.17
I_2° solid $+ 12OH^-$	10	$2IO_3^- + 6H_2O$	−0.21
$Ag^\circ + Cl^-$	1	$AgCl$	−0.23
Hg_2Cl_2 solid $+ 2Cl^-$	2	$2HgCl_2$	−0.24
$I^- + 6OH^-$	6	$IO_3^- + 3H_2O$	−0.26
As°	3	As^{+++}	−0.29
Bi°	3	Bi^{+++}	−0.30
Cu°	2	Cu^{++}	−0.34
$Ag^\circ + 2NH_3$	1	$Ag(NH_3)_2^+$	−0.38
Co°	3	Co^{+++}	−0.40
$4OH^-$	4	O_2 gas $+ 2H_2O$	−0.41
Sb°	3	Sb^{+++}	−0.47
Br° liq. $+ 6OH^-$	5	$BrO_3^- + 3H_2O$	−0.51
Cu°	1	Cu^+	−0.51
Br_2 liquid $+ 12OH^-$	10	$2BrO_3^- + 6H_2O$	−0.51
MnO_2 solid $+ 4OH^-$	3	$MnO_4^- + 2H_2O$	−0.52
$2I^-$	2	I_2 solid	−0.53
$Br^- + 6OH^-$	6	$BrO_3^- + 3H_2O$	−0.60
Fe^{++}	1	Fe^{+++}	−0.75
Ag°	1	Ag^+	−0.80
$2Hg^\circ$	2	Hg_2^{++}	−0.80
H_2O_2	2	O_2 gas $+ 2H^+$	−0.80

* Values obtained from Landolt-Bornstein *Physikalisch-chemische Tabellen*, 1912, and Noyes, *Qualitative Chemical Analysis*, 1920.

† These values denote the reduction potentials for the unknown concentrations of ions in molal $SbCl_3$, $SnCl_2$ and H_2SnCl_6 solutions in the presence of normal HCl. The reduction potentials cannot be given for molal concentrations of the ions Sb^{+++}, and Sn^{++++} as the extent of ionization and of complex formation in antimony and tin chloride solutions are not known accurately

REDUCTION POTENTIALS IN MOLAL SOLUTIONS.—*Cont.*

Original State.	Increase in Valence.	Oxidized State.	E.m.f. in volts.
$Cl_2°$ gas$+2OH^-$	2	$2HClO$	−0.85
$Hg°$	2	Hg^{++}	−0.86
$2Hg^+$	2	$2Hg^{++}$	−0.92
$2Br^-$	2	Br_2 liquid	−1.08
Cl^-+OH^-	2	$HClO$	−1.10
I_2 solid$+6OH^-$	10	$2IO_3^-+6H^+$	−1.19
$Cr^{+++}+4H_2O$	3	$HCrO_4^-+7H^+$	−1.3
$Mn^{++}+2H_2O$	2	MnO_2 solid$+4H^+$	−1.35
$2Cl^-$	2	Cl_2 gas	−1.35
$Pb^{++}+2H_2O^-$	2	PbO_2 solid$+2H^+$	−1.44
$Au°$	1	Au^+	−1.5
Cl^-+H_2O	2	$HClO+H^+$	−1.51
$Mn^{++}+4H_2O$	5	$MnO_4^-+8H^+$	−1.52
MnO_2 solid$+2H_2O$	3	$MnO_4^-+4H^+$	−1.63
$2H_2O$	2	$H_2O_2+2H^+$	−1.66
Cl_2 gas$+2H_2O$	2	$2HClO+2H^+$	−1.67
Co^{++}	1	Co^{+++}	−1.8
Cl_2 gas$+2OH^-$	2	$2ClO^-+2H^+$	−1.8
O_3 gas$+H_2O$	2	O_3 gas$+2H^+$	−1.9
$2F^-$	2	F_2 gas	−1.96

Lead and tin occupy neighboring positions in the series. In a neutral solution, therefore, lead will precipitate tin from a solution containing stannous ions. As the concentration of the lead ions increases and the concentration of the stannous ions decreases, the reduction potentials approach one another so that equilibrium is soon reached. Conversely, when no stannous ions are present, metallic tin will precipitate a little lead from a solution containing lead ions, but the equilibrium will soon be reached. The presence of acid, however, will stop both of these reactions. On the other hand, the reduction potential of stannous to stannic tin, although not given in the table, has a negative value, and the lead will reduce stannic ions even in the presence of acid.

All reactions of oxidation and reduction represent reversible reactions. The strong reducing agents on being oxidized become weak oxidizing agents, and conversely the strong oxidizing agents on being reduced become weak reducing agents. Ordinarily hydrogen is considered a reducing agent, but when a metal replaces the hydrogen of an acid, hydrogen ions act as the oxidizing agent.

The mass-action law holds for oxidation and reductions as for all other chemical reactions that take place in solution; when the reduction voltages are far apart, however, the reaction of oxidation and reduction will apparently go to completion.

We shall now turn aside from reactions of oxidation and reduction and consider some further applications of the mass-action law as applied to reactions that are of importance in analytical chemistry.

The Effect of a Common Ion

The exact extent to which the ionization of concentrated solutions of highly ionizable salts takes place, is not yet positively known. Many facts indicate that neutral salts and largely ionized acids and bases of the univalent type are completely ionized even in quite concentrated aqueous solutions. Often ionization values are calculated from electrical conductance ratios, as in the table on page 10, but it has been found that such values do not change with dilution in accordance with the mass action law. In concentrated solutions, the mobility of the ions is undoubtedly less than in dilute solutions and a certain resistance to the passage of the ions through a solution under the influence of an electric current is caused by the tendency of positive electrified particles to attract negatively charged particles and *vice versa*. Such factors are disregarded, as a rule, in determining ionization by the conductivity method. In all applications of the mass action law to the different types of equilibrium between dissolved substances it is best to assume, therefore, that *highly ionized substances are completely ionized even in concentrated solutions*. When a solution of a salt such as sodium chloride is treated with the solution of a salt with a common ion, such as sodium nitrate or potassium chloride, the resulting effect upon the chemical nature of the dissolved sodium chloride is scarcely noticeable.

The relations are quite different when one of the original substances is difficultly soluble or only slightly ionized. Thus when a precipitate of silver chloride is formed, the solution is saturated with the salt and the solubility product of the ions has been reached. If now a small amount of either chloride or silver ions is added to the saturated solution of silver chloride, further precipitation of silver chloride should take place. In general, therefore, a slight excess of precipitant will make a precipitate less soluble. There are exceptions to this rule, however. The rule does not hold if one of the ions from the precipitate shows a tendency to form a soluble complex ion with the excess of precipitant. Thus silver chloride is, in fact, less soluble in very dilute sodium chloride solution than it is in water, but it dissolves in a saturated brine solution more than in pure water, probably owing to the formation of a complex ion. Barium sulfate is less soluble in dilute sulfuric acid than it is in water, but concentrated sulfuric acid dissolves it quite readily. Aluminium hydroxide is precipitated by

the very careful neutralization of an aluminium salt, but the hydroxide dissolves in sodium hydroxide solution, forming sodium aluminate. None of these examples is contrary to the mass-action law, but they show the need of considering all the possible reactions.

When a weak electrolyte is present in solution, the effect of the common ion is often quite remarkable. To illustrate this effect let us consider the weak electrolytes acetic acid, hydrogen sulphide and ammonium hydroxide. The table on page 10 shows that a 0.1 N solution of acetic acid is dissociated to between 1 and 2 per cent. The value of the ionization constant at 18° is about 0.000018. From this value, the ionization (x) in 0.1 N solution can be computed as follows:

$$\frac{x_2}{0.1 - x} = 0.000018; \quad x = 0.00134 = 1.34 \text{ per cent.}$$

The table on page 10 shows that the salts of the type represented by sodium acetate are dissociated to about 84 per cent. A liter of 0.1 N sodium acetate solution contains, therefore, 0.084 mole of acetate ions, whereas one of 0.1 N acetic acid contains only 0.0013 mole of acetate ions. When enough solid sodium acetate is added to 0.1 N acetic acid to make the solution 0.1 N with respect to both the acid and the salt, the common acetate ion tends to repress the ionization of both the original molecules; the total concentration of acetate ion is increased only very slightly and we are justified in assuming that 0.084 represents with sufficient accuracy the concentration of the acetate ion. The concentration of the hydrogen ions may be designated again as x and that of the non-ionized acetic acid as $0.1 - x$. The ionization constant of acetic acid remains the same and the mass-action expression becomes

$$\frac{0.084\,x}{0.1 - x} = 0.000018; \quad x = 0.000021 = 0.02 \text{ per cent.}$$

By adding an equivalent weight of sodium acetate, therefore, the ionization of 0.1 N acetic acid is changed from 1.3 per cent to 0.02 per cent.

The effect of ammonium salt upon the ionization of ammonium hydroxide is similar. The table on page 22 gives the solubility product of ferric hydroxide as 1.1×10^{-36} and that of magnesium hydroxide as 3.4×10^{-11}. As the cube of the OH^- concentration is taken in computing the solubility product of ferric hydroxide and only the square of this concentration in the case of magnesium hydroxide, the difference in solubilities is not as great as these solubility products would indicate, but the values show that it takes only an extremely low concentration of hydroxyl ions to satisfy the solubility product of ferric hydroxide and many times as much to

satisfy that of magnesium hydroxide. Ammonium hydroxide added to a solution containing ferric and magnesium ions will cause the precipitation of both iron and magnesium as hydroxide, but by adding sufficient ammonium chloride to the solution, the ionization of the base is repressed, exactly in the same way that sodium acetate acted upon acetic acid, to such an extent that none of the magnesium is precipitated although the precipitation of the iron remains practically complete.

The effect of hydrogen ions upon the ionization of hydrogen sulfide is similar. The solubility product of copper sulfide is 8.5×10^{-45} and that of zinc sulfide is 1.2×10^{-23}. The precipitation of both copper and zinc by hydrogen sulfide is practically complete in a solution containing no excess hydrogen ions. As the metal precipitates, however, hydrogen ions are formed:

$$Zn^{++} + H_2S \rightarrow \mathbf{ZnS} + 2\,H^+.$$

The accumulation of these hydrogen ions serves to repress the ionization of hydrogen sulfide and tends to stop the precipitation of the zinc. If, therefore, we wish to precipitate copper and leave zinc in solution, all that is necessary is to add a little acid at the start; in 0.3 N acid solution the precipitation of the copper as sulfide is practically complete, while little if any zinc sulfide is precipitated. On the other hand, if some sodium acetate is added to the solution, non-ionized acetic acid is formed and the accumulation of the hydrogen ions is prevented. This effect is so remarkable that it is easier to precipitate zinc sulfide from a solution containing acetic acid and sodium acetate than from a solution of zinc chloride in water. The concentration of hydrogen ions is kept very low, even although the solution may smell strongly of non-ionized acetic acid.

The common ion effect is also involved in the dissolving of precipitates. The effect is shown, for example, when calcium phosphate is dissolved by acid. The table on page 10 shows that the tertiary ionization of phosphoric acid is about the same as the secondary ionization of hydrogen sulfide and the secondary ionization is comparable to the primary ionization of hydrogen sulfide. If many hydrogen ions are added in the form of a mineral acid, the ionization of HPO_4^{--} and of $H_2PO_4^-$ becomes extremely small. The saturated solution of calcium phosphate contains Ca^{++} and PO_4^{---} ions. These PO_4^{---} ions must be in equilibrium with added hydrogen ions. When the PO_4^{---} from HPO_4^{--} is kept less than the PO_4^{---} concentration corresponding to the value of a saturated solution of calcium phosphate, the calcium phosphate must tend to dissolve. As $Ca(H_2PO_4)_2$ is much

more soluble than $CaHPO_4$, which in turn is more soluble than $Ca_3(PO_4)_2$, it is desirable to add enough acid to make the $H_2PO_4^-$ practically non-ionized.

The common ion effect which is involved in nearly every reaction of precipitation and of dissolution represents an application of the mass-action principle.

Hydrolysis

Hydrolysis is the name given to the decomposing action of water upon salts.* Corresponding to the fact that water is a poor conductor of electricity, it follows that water is ionized only to a slight extent.

$$H_2O \rightleftarrows H^+ + OH^-.$$

According to Kohlrausch and Heidweiler,† the degree of ionization at 25° C. is 1.05×10^{-7}; in other words, about 10,000,000 liters of water would furnish 1 mole of ionized water or 1 mole of hydrogen ions.‡ Small as this is, it suffices to explain the hydrolysis of:

I. The salts of weak acids with strong bases.
II. The salts of strong acids with weak bases.
III. The salts of weak acids with weak bases.
IV. The salts of strong acids with strong bases are not hydrolyzed appreciably.

Hydrolysis is shown to take place by the fact that solutions of neutral salts corresponding to I react alkaline, those of II react acid, while those of III are sometimes acid and sometimes alkaline.

The cause of hydrolysis is the action of the ions of water upon the ions of the dissolved salt.

All monobasic salts in aqueous solution are largely ionized (cf p. 10):

$$RA \rightarrow R^+ + A^-,$$

and the phenomenon of hydrolysis may be represented by the general equation

$$\underbrace{R^+ + A^-}_{\text{Salt}} + H_2O \rightleftarrows \underbrace{ROH}_{\text{Base}} + \underbrace{HA}_{\text{Acid}}.$$

In formulating mass-action expressions involving highly ionized and slightly ionized substances it has been found best to employ the

* Certain organic substances which are not salts are also subject to hydrolysis.

† *Z. phys. chem.*, **14**, 317.

‡ Since 1 mole of water when ionized furnishes 1 mole of H^+ and one mole of OH^-, it follows that the ionization of 1.05×10^{-7} moles of water furnish 1.05×10^{-7} moles of H^+ and an equal quantity of OH^- ions. Moreover, in any aqueous solution, $[H^+] \times [OH^-]$ will equal 1.05×10^{-14}.

concentration of the *ions* of *highly* ionized substances, and the concentrations of the *non-ionized* portions of *slightly* ionized substances. Since in dilute solutions the mass of the water changes inappreciably when the reaction takes place, we may neglect it in the formulation.

There are now three typical equations which represent the application of the mass-action principle to the hydrolysis of the above three classes of salts.

I. Hydrolysis of Salts of Weak Acids and Strong Bases

The base formed by the hydrolysis is largely ionized, while the acid is only slightly so. The mass-action equation now takes the form

$$(1)\quad K_h = \frac{[R^+][OH^-][HA]}{[R^+][A^-]} = \frac{[OH^-][HA]}{[A^-]} = \frac{K_w}{K_{HA}}.^*$$

Owing to the presence of the OH^- ions in appreciable amount, all salts of this category react alkaline. The alkali salts of hydrocyanic acid, hypochlorous acid, carbonic acid, boric acid, and hydrogen sulfide are of this type.

II. Hydrolysis of Salts of Strong Acids and Weak Bases

Here the conditions are reversed, and it is the acid which is almost completely dissociated and the base but slightly. In this case the formula becomes

$$(2)\quad K_h = \frac{[ROH][H^+][A^-]}{[R^+][A^-]} = \frac{[ROH][H^+]}{[R^+]} = \frac{K_w}{K_{ROH}}.$$

Salts of this class, such as those of chromium, aluminium, iron, etc., react acid when in aqueous solution.

In the case of polyvalent bases hydrolysis takes place in stages:

$$RCl_2^+ + H_2O \rightleftarrows RCl_2OH + H^+$$
$$RCl^{++} + 2\,H_2O \rightleftarrows RCl(OH)_2 + 2\,H^+$$
$$R^{+++} + 3\,H_2O \rightleftarrows R(OH)_3 + 3\,H^+.$$

Ferric, aluminium and chromic chlorides, for example, react acid in aqueous solution. If such solutions be evaporated to dryness, considerable hydrochloric acid is volatilized, and the residue obtained is an insoluble basic salt which can only be dissolved by means of acid.

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* In these expressions K_w, K_{HA}, and K_{ROH} denote the ionization constants of water, the weak acid and the weak base.

III. Hydrolysis of Salts of Weak Acids and Weak Bases

The acids and bases formed by hydrolysis are only slightly dissociated, but to different extents. Our formula becomes

$$(3)\quad K_{h''} = \frac{[ROH][HA]}{[R^+][A^-]} = \frac{K_w}{K_{HA} \cdot K_{ROH}}.$$

Salts of this type are especially subject to hydrolysis and, as both the acid and base are slightly ionized, the hydrolysis may take place to a considerable extent without the solution manifesting either acid or basic properties.

If the electrolytic dissociation of the acid is greater than that of the base, the solution reacts acid; and conversely, when the base is stronger than the acid the solution of the salt shows an alkaline reaction.

Neutral ferric acetate in a *boiling*, aqueous solution is hydrolyzed:

$$Fe(C_2H_3O_2)_3 + 2\,H_2O \rightleftarrows Fe(OH)_2C_2H_3O_2 + 2\,HC_2H_3O_2.$$

Basic ferric acetate is precipitated and can be removed by filtering the hot solution. If the solution is allowed to cool, the reaction tends to take place in the reverse direction and some of the basic salt goes into solution. *Heat and dilution always favor hydrolysis.**

IV. Hydrolysis of Salts of Strong Acids with Strong Bases

Salts of this type yield, by hydrolysis, acids and bases which are almost entirely dissociated in dilute aqueous solution, and the general equation becomes:

$$K_{h'''} = \frac{[R^+][OH^-][H^+][A^+]}{[R^+][A^-]} = [H^+][OH^-].$$

The H^+ and OH^- ions, however, are in equilibrium with undissociated water; the solution reacts neutral and contains only as many H^+ and OH^- ions as correspond to the ionization of water, which is so small that there remains only the electrolytic dissociation of the salt to be considered. *Salts of this type are not subject to appreciable hydrolysis.*

The hydrolytic action of water, as well as the mass-action law, may be illustrated by the following experiment: A little water, added

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* The ionization constant for water is $0.0_{13}12$ at 25° but rises to $0.0_{11}5$ at 100°. The water is, therefore, much more dissociated at the higher temperature and as a result the hydrolysis is favored.

to a solution of antimony chloride in concentrated hydrochloric acid causes precipitation of antimony oxy-chloride:

$$Sb\begin{matrix}\diagup Cl \\ - Cl \\ \diagdown Cl\end{matrix} + \begin{matrix}H \diagdown \\ H \diagup\end{matrix} O \rightleftarrows Sb\begin{matrix}\diagup O \\ \diagdown Cl\end{matrix} + 2\,HCl,$$

which dissolves on adding a little concentrated hydrochloric acid. Further addition of water again precipitates the basic salt, which will dissolve in more of the concentrated acid, etc. It is obvious that by increasing the mass action of the water the reaction goes from left to right, while by increasing the concentration of the hydrochloric acid it goes from right to left.

The analytical chemist frequently desires to assist or to prevent hydrolysis. The mass-action principle shows how this can be done. To assist a chemical reaction it is necessary to increase the concentration of one of the original reacting substances or to lessen the concentration of one of the substances formed. Aside from the reactions of oxidation and reduction, all the reactions that take place completely in aqueous solution are those in which the concentration of one of the substances formed is practically negligible. This is due to the formation of (1) a precipitate, (2) a gas, or (3) an undissociated substance (cf. p. 26). Neutralization takes place between an acid and a base because of the tendency to form undissociated water. Hydrolysis is the reverse of neutralization and is due to the fact that water is slightly dissociated. Hydrolysis takes place when one of the products is a gas, a precipitate, or an undissociated substance. Thus the hydrolysis of a salt of a weak acid and a strong base is due to the fact that the dissociation of the weak acid is slight. The hydrolysis of a salt of a strong acid and a weak base is due to the formation of the undissociated base. Hydrolysis takes place most readily when both the acid and the base are weak, because then both the H^+ ions and the OH^- ions are removed from the solution to form undissociated acid and undissociated base. Hydrolysis of a salt of a strong acid and a strong base cannot take place because there is then no tendency for the H^+ and OH^- ions of water to be removed. To assist hydrolysis, boiling is advisable, because the water is so much more dissociated at this temperature than when cold. The reaction that takes place on boiling often proceeds in the other direction on cooling, simply on account of the change in the ionization of the water itself. Dilution favors hydrolysis because it diminishes the concentration of the substances formed; the concentration of the ions from water is not changed, but the relative proportions of these ions to other ions present is increased.

Hydrolysis is also favored when one of the products is gaseous or insoluble; thus ammonium carbonate is very easily hydrolyzed, because both ammonia and carbon dioxide are volatile, and ferric acetate is hydrolyzed not only because the acid and base are both weak, but the basic ferric acetate is also very insoluble. Finally, to stop hydrolysis it is only necessary to add a little free acid or free base at the start, and the efficiency of the acid or base is proportional to the extent to which it is itself ionized. If the solution becomes alkaline as a result of hydrolysis, then a little alkali will best stop hydrolysis, but if the solution becomes acid, a little acid should be added. Moreover, it is advisable to work in cold and concentrated solutions. A dilute aqueous solution of potassium cyanide has the odor of free hydrocyanic acid and reacts alkaline to litmus, but if a little caustic potash is added, the hydrolysis of the salt is prevented and the odor of hydrocyanic acid can be detected no longer. Similarly, boiling a solution of neutral ferric sulfate results in the precipitation of a basic salt, but the precipitation does not take place if a little sulfuric acid is added at the start.

Amphoteric Electrolytes

According to ideas that prevailed nearly a century ago, an acid was regarded as composed of a *negative element* and hydroxyl; a base was regarded as composed of a *positive element* and hydroxyl. According to the modern conception, an acid is a substance capable of yielding hydrogen ions and a base is a substance capable of yielding hydroxyl ions. The so-called *negative elements* are sometimes simple negatively-charged ions, as the Cl^- of hydrochloric acid, and sometimes complex anions, such as the SO_4^{--} of sulfuric acid, containing a positively charged element and negatively charged oxygen.

The extent to which the ionization takes place in the solution of an acid or a base varies greatly. In 0.1 N solution, the table on page 10 shows that some acids and some bases are dissociated to about 90 per cent, while other acids and other bases are dissociated to 1 per cent or less. We are accustomed to regard the strength of an acid or of a base as shown by the extent to which ionization takes place in aqueous solution.

As a general rule, when the positive charge on an element is increased, the more difficult it becomes for the corresponding hydroxide to ionize as a base and the greater the tendency for the hydroxide to ionize as an acid. Thus the higher the positive charge on the atom, the more *negative* it becomes according to the old-fashioned conception. This apparent contradiction is not quite as inconsistent

as it seems; it arises from a confusion of the *intensity* factor of electric energy with the *quantity* factor. All forms of energy are composed of these two factors and such confusion of the factors is quite common.

The quantity of electricity corresponding to a unit electric charge on a gram atom of any element is 96,500 coulombs. All univalent elements bear this charge and all bivalent elements twice as much. On the other hand, the tendency of the atoms to accept or give up electrons varies greatly, as the table of reduction potentials shows (p. 44). It is customary to speak of the elements which show the greater tendency to give up one or more electrons of negative electricity as more positive than those which show less tendency to lose electrons. In other words, the elements nearer the top of the electromotive series are regarded as more positive than those which are below them in this series. Thus the older conception of positive and negative nature was largely one of electromotive force, or voltage, rather than one of electric nature or quantity of electricity. It corresponds to the behavior of the element in an electric couple such as that of the Daniell cell; the zinc becomes the anode in such a cell and the copper the cathode; the current flows through the cell from the zinc to the copper and it is customary to say that the zinc is positive to the copper *in the solution*. The student should be careful to distinguish in his own mind the difference between the meaning of the word positive when used in this sense of voltage and when used to represent the character of an electric charge.

Water is a substance which ionizes to a slight extent and the initial products of the ionization are H^+ and OH^-. Water, therefore, may be considered as being both an acid and a base. There are other substances which act as acids without forming at one time any more hydrogen ions than does water and other basic substances which do not form more hydroxyl ions. Water is characterized by the fact that it forms an equal amount of both hydrogen and hydroxyl ions by its primary ionization. Other hydroxides are known which have both acid and basic properties, but this is due to two distinct kinds of ionization. At one time they dissociate as an acid and at another time as a base. Such substances are said to be *amphoteric electrolytes*.

Aluminium hydroxide is an amphoteric electrolyte. This substance has a very small solubility product and the quantity of ions present in the saturated solution is extremely small. The chemical behavior of aluminium hydroxide shows, however, that it is capable of dissociating in two ways:

$Al(OH)_3 \rightarrow Al(OH)_2^+ + OH^-$ (ionization as a base);

$Al(OH)_3 \rightarrow H^+ + AlO_3H_2^- \rightarrow H^+ + AlO_2^- + H_2O$ (ionization as an acid).

The mass-action principle enables one to predict which of these ionization reactions will take place. In the presence of a strong acid, such as hydrochloric acid, the common ion effect of the hydrogen ions will prevent the ionization of the aluminium hydroxide as an acid; the effect is much more marked than that of sodium acetate upon acetic acid, for in this case the difference in the percentage ionization of hydrochloric acid and aluminic acid is much greater. On the other hand, the presence of the hydrogen ions favors the ionization of the aluminium hydroxide as a base. To establish the proper equilibrium between H^+, OH^- and H_2O, nearly all the OH^- ions from the aluminium hydroxide react with the H^+ of the hydrochloric acid. On account of this removal of the OH^-, the ionization of the $Al(OH)_3$ progresses, the $Al(OH)_2^+$ ionizes into $Al(OH)^{++}$ and OH^- and finally the $Al(OH)^{++}$ ionizes into Al^{+++} and OH^-. In this way $Al(OH)_3$ dissolves to form $AlCl_3$.

Similarly, in the presence of sodium hydroxide, the common ion effect of the OH^- prevents the aluminium hydroxide from ionizing as a base and the H^+ ions formed by its dissociation as an acid react with the OH^- ions from the sodium hydroxide, and the final result is that the aluminium all dissolves as sodium aluminate, $NaAlO_2$.

Whenever an oxide or hydroxide dissolves by chemical reaction with an acid, and also by chemical reaction with a base, the substance is obviously an amphoteric electrolyte.

Detection of Acids and Bases. Theory of Indicators[*]

To detect the presence of free hydrogen cations or of hydroxyl anions, certain colored, organic substances are used, called *indicators*. These indicators are very weak acids, very weak bases or amphoteric electrolytes and the free acid, or base, is an unstable substance which tends to undergo a slight rearrangement of the atoms in order to assume a condition of greater stability. The color of any organic compound is due to a certain special arrangement of certain atoms, the *chromophor;* when this arrangement is changed, the color is also changed or lost.

Methyl orange is an amphoter and is capable of forming salts with both acids and bases, but its indicator characteristics are due to its very weak basic properties. The neutral solution of its sodium salt is used as an indicator. In this sensitive neutral solution we have

[*] Cf. J. Stieglitz, *J. Am. Chem. Soc.*, **25**, 1117; **39**; Acree, *ibid.*, **37**, 39, 42; McCoy, *ibid.*, **31**, 508; Salm, *Z. phys. Chem.*, **57**, 471; and A. A. Noyes, *J. Am. Chem. Soc.*, **32**, 815.

a condition of equilibrium between the two isomeric forms of methyl orange as expressed by the equation

$$HSO_3 \cdot C_6H_4N : N \cdot C_6H_4N(CH_3)_2 \rightleftarrows SO_3C_6H_4NH \cdot N : C_6H_4 : N(CH_3)_2.$$

The compound on the left is yellow in color and its color is due to the azo group N : N; the other compound is red, having for its chromophor the quinoid group : C_6H_4 : .

The sodium salt of methyl orange is yellow and has the formula

$$NaSO_3 \cdot C_6H_4N : N \cdot C_6H_4N(CH_3)_2,$$

and when decomposed by acids the free sulphonate

$$SO_3 \cdot C_6H_4NH \cdot N : C_6H_4 : N(CH_3)_2$$

is formed, which is red.

The red quinoid form is ionized as a weak base and forms red salts with acids. It does not form salts readily with weak acids, such as carbonic or acetic acid, because, as we have seen, salts of weak bases and weak acids are hydrolyzed. This is why methyl orange is not a sensitive indicator for weak acids. As a very weak base it will be driven readily out of its red salts by other bases, even weak ones; and the free base will revert again to its yellow form, the result being that methyl orange is an excellent indicator for weak bases.

Phenolphthalein, another valuable indicator, is a very weak acid. The free acid, however, is unstable, and when set free from one of its colored salts reverts instantly into a colorless lactoid form:

$$\underset{\text{Red}}{HOOCC_6H_4C(C_6H_4OH) : C_6H_4 : O} \rightleftarrows \underset{\text{Colorless}}{OOCC_6H_4C(C_6H_4OH)_2}.$$

The red color is in this case also due to the quinoid grouping : C_6H_4 :. In the free acid, the condition of equilibrium favors the lactoid form, and only minimal quantities of the quinoid acid are present. This trace of quinoid acid is ionized and in equilibrium with its ions:

$$HOOCC_6H_4C(C_6H_4OH) : C_6H_4 : O \rightleftarrows H^+ + OOCC_6H_4C(C_6H_4OH) : C_6H_4 : O^-.$$

The addition of an alkali causes the hydrogen ions to disappear, more of the quinoid molecules must be ionized to preserve equilibrium, and the quinoid molecules in turn be reproduced from the lactoid as fast as the former are converted into the salt. Phenolphthalein is a very sensitive indicator toward acid, but on account of being such a weak acid it does not form stable salts with weak bases.

Besides these indicators, others are often employed, among which may be mentioned **Litmus** and **Lacmoid,** which are red with acids and blue with alkalies; and **Turmeric,** which is brown with alkalies and yellow with acids.

The various indicators, therefore, differ from one another with regard to the extent to which they normally undergo ionization either as an acid or as a base. They show, as a result, specific degrees of sensitiveness to hydrogen cations and to hydroxyl anions. The following table shows the concentration of the ion required to produce the color change. The table gives results obtained when about two drops of a 0.1 per cent solution of the indicator are added to 10 cc. of the solution tested.

SENSITIVENESS OF INDICATORS*

Indicator.	Color with H^+.	Color with OH^-.	Concentration Required† for Color Change of	
			H^+.	OH^-.
Phenolphthalein	colorless	pink	$0.0_7 1$	$0.0_4 1$
Azolitmin (in litmus)	violet pink	violet	$0.0_8 1$	$0.0_6 1$
Methyl orange	reddish-orange	yellow	$0.0_2 1$	$0.0_8 1$

The table shows that of these three indicators phenolphthalein is the most sensitive to acids, and methyl orange is the most sensitive to bases.

Colloidal Solutions

If an alkaline silicate in dilute solution is mixed with dilute hydrochloric acid, the solution remains clear and apparently unchanged in spite of the fact that silicic acid is only slightly soluble in water. If the liquid thus obtained is placed in a vessel whose walls are formed of parchment paper or of bladder, and this vessel is placed in pure water, it is possible to wash out all the excess hydrochloric acid and all of the sodium in the form of sodium chloride. This is the so-called process of dialysis. The liquid in the dialyzer contains silicic acid.

The silicic acid, however, is not in the form of a true solution. If it is evaporated, an amorphous, gelatinous mass is obtained which is only

* From J. Stieglitz: Qualitative Analysis.

† Since $[H^+] \times [OH^-] = 1.05 \times 10^{-14}$ in any solution, the OH^- concentration is $0.0_6 1$ when the H^+ concentration is $0.0_7 1$, $0.0_7 1$ when $[H^+]$ is $0.0_4 1$ and $0.0_{10} 1$ when $[H^+]$ is $0.0_2 1$. The first column in the table indicates when acid *begins* to affect the indicator and the second column when a base *begins* to affect it.

slightly soluble in water. The boiling-point and freezing-point of the solution do not differ much from that of pure water. The addition of various substances, especially of salts, causes the liquid to solidify as a jelly, especially if it has been concentrated somewhat by evaporation in the cold.

A similar experiment can be performed with arsenious acid and hydrogen sulfide. The aqueous solution of arsenious oxide turns orange yellow when hydrogen sulfide is passed into it and becomes opalescent without forming any precipitate, although arsenious sulfide is only very slightly soluble in water. The liquid will pass unchanged through an ordinary paper filter. If a little hydrochloric acid or some salt solution is added to the yellow opalescent liquid, a heavy precipitate of arsenious sulfide at once forms.

A liquid in which a very insoluble substance appears to be in solution far beyond its usual degree of solubility, and yet does not show at all the behavior of an ordinary supersaturated solution, is said to contain the substance in *colloidal solution.*

Such solutions are very commonly formed with difficultly soluble gelatinous substances. It was formerly thought that such solutions represented true solutions of difficultly soluble substances in the form of a soluble colloidal modification, but more recent observations with the ultramicroscope have indicated that colloidal solutions are really suspensions of minute solid particles. The colloidal condition evidently interferes with the precipitation of insoluble substances, and since most of the separations of analytical chemistry depend on the formation of precipitates, analytical chemistry is chiefly concerned with the colloidal condition as one that is to be avoided as much as possible.

The suspended particles of most colloids carry electrical charges; a potential difference exists between the particles and the liquid. Sometimes the charge on the particles is positive, as with the colloidal solution of ferric hydroxide, aluminium hydroxide and chromium hydroxide and sometimes the charge is negative, as with the colloidal solutions of silicic acid, stannic acid, the sulfides of arsenic and cadmium, silver iodide, silver chloride, gold, platinum and silver. Substances in the colloidal condition which carry an electric charge are precipitated by an electrolyte. Negatively-charged colloids are precipitated by the action of positive ions and, conversely, the positively-charged colloids are precipitated by negative ions. The precipitated substance carries with it a little of the precipitating ion in the form of an adsorption compound. The precipitating power of electrolytes increases decidedly with the valence of the precipitating ion.

Some colloids do not carry much of an electric charge and sometimes

the charge is positive in acid and negative in alkaline solutions. Colloids which do not carry much electric charge are not precipitated by dilute solutions of electrolytes. These colloids are coagulated by heat by any other method of dehydration such as the addition of concentrated salt solutions, or by the addition of another solvent such as alcohol. Colloids which are not sensitive to precipitation by electrolytes often act as protective colloids and hinder the precipitation of other substances. Thus tannic acid, gelatin and albumin act as such protecting agents, probably by forming protective films.

To prevent the colloidal condition in analytical work it is necessary to take certain precautions. Since electrolytes cause the precipitation of colloids, it may be expected that their absence will tend to aid in the formation of colloidal solutions. Thus in washing a precipitate which is known to have a tendency to pass into colloidal solution, it is best to wash with a solution of some indifferent electrolyte rather than with pure water. Again, if precipitations are attempted in very dilute solutions of such substances as arsenious sulfide, it is best to have an electrolyte in the solution at the start. It is also necessary to remember that the colloids carry down with them the precipitating ion by which they are coagulated. To avoid analytical mistakes caused by such loss of ions, a sufficient concentration of some other ion is usually provided in the form of an acid or an ammonium salt. The washing of the precipitated colloid with ammonium chloride or ammonium nitrate gradually removes these precipitated ions, but it is very difficult to avoid all danger of loss from this source.

When protective colloids, especially of the gelatin or albumin type are present, they may interfere so much with the common precipitation tests that it is necessary to destroy the protective colloid, usually by oxidation, before proceeding with the analysis.

The Evaporation of Acids

It is often necessary to diminish the acid concentration of a solution. The simplest way to accomplish this is by neutralization, but it is often undesirable to introduce foreign substance into the solution, and in such cases the acid is removed by evaporation. To prevent loss by spattering, it is well to evaporate in a porcelain dish on the steam bath; but, to save time, the evaporation may take place over a free flame. In this case the solution should be kept in motion either by stirring or by rotating the contents of the dish and moving it back and forth over the flame. For evaporations over a free flame, an Erlenmeyer flask is often used; the sides of the flask, being cooled by the air, act as a condenser and delay evaporation but they also serve to

prevent mechanical loss. Spattering is caused by steam being formed too rapidly at the bottom of the dish, by steam being formed beneath a crust which has formed on the surface of the liquid, or by steam being formed from enclosed mother-liquid in a solid that has separated. The steam escapes then only after its pressure has become considerable. The breaking of glass dishes when heated over a free flame is due to overheating the glass by contact of the flame with some part that is not being kept relatively cool by contact with liquid. Moving the vessel back and forth over the flame prevents breakage by preventing overheating of the glass; the bottom is kept uniformly wet on the inside even when but little liquid remains.

The behavior of acids upon evaporation is interesting. A solution of hydrochloric acid of specific gravity 1.10 boils at 110° under atmospheric pressure. The solution contains 20.2 per cent of hydrogen chloride and its concentration is thus a little less than 6 N. No other mixture of water and hydrochloric acid boils as high and consequently in evaporating a solution of hydrochloric acid, although the total quantity of hydrochloric acid constantly diminishes, the concentration of the remaining acid will tend to approach the composition of the constant boiling mixture. If the acid is more dilute at the start, evaporation will cause the acid that remains to be more concentrated, and if more concentrated at the start, evaporation will cause the remaining acid to be more dilute.

Nitric acid similarly forms a constant boiling mixture with water. This mixture boils at 120.5° and contains 68 per cent of nitric acid; the acid concentration of the mixture is about 15.5 N.

Sulfuric acid forms with water a constant boiling mixture that contains 98.3 per cent of anhydrous sulfuric acid and boils at 330°. It was once thought that these constant boiling mixtures of acid and water corresponded to definite hydrates of the acid, but the composition of such a mixture and the boiling-point varies with changes in pressure in a way that proves no definite compound is present.

When it is desired to change a solution of a chloride to one of a nitrate it is very easy to do this by evaporating once or twice with nitric acid. The nitric acid reacts with the hydrochloric acid,

$$6\,HCl + 2\,HNO_3 = 4\,H_2O + 2\,NO\uparrow + 3\,Cl_2\uparrow,$$

and by adding an excess of the nitric acid all of the chloride is decomposed. The most economical way to accomplish the change is to evaporate nearly to dryness and then add a little strong nitric acid, repeating the evaporation and addition of acid until no more red fumes are evolved on adding the acid (NO + air = red NO_2).

Similarly a solution of nitric acid may be changed to one of hydro-

chloric acid. Aqua regia is formed, as in the above case, and by using an excess of hydrochloric acid all the nitrate is decomposed.

The replacement of nitric acid or of hydrochloric acid by sulfuric acid is based on another principle. In this case the change is accomplished by evaporating till dense fumes of sulfuric acid are evolved. Very little sulfuric acid is lost until all of the more volatile acid has evaporated.

Phosphoric acid is still less volatile. By evaporation with phosphoric acid even sulfuric acid can be distilled off without losing an appreciable quantity of phosphoric acid, but the phosphoric acid is changed to pyrophosphoric acid or to metaphosphoric acid.

To change a sulfate or a phosphate solution to a chloride or nitrate presents a more difficult problem than that of simple evaporation. It is customary in such cases to remove the phosphate or sulfate ions by precipitation or to precipitate the desired cation as hydroxide or carbonate and to dissolve the precipitate in the desired acid.

Filtration and Washing of Precipitates

When a precipitate is produced in qualitative analysis it is necessary to remove it from the liquid by means of *filtration*. The size of the filter used should be determined by the size of precipitate and not by the volume of liquid. In attempting to detect the presence of traces of a substance it is often necessary to work with large quantities of the original substance, and this involves the use of correspondingly large volumes of liquid. If from such a solution a very little precipitate is formed, it will be practically lost if spread over a large filter, and further work with the precipitate is hampered.

Before examining such a precipitate it must be completely freed from all traces of the filtrate. This is accomplished by *washing*. Washing must be continued until no test can be obtained with the wash-water for a certain substance known to be present in the filtrate. For example, suppose it is necessary to filter off some suspended barium sulfate from a solution containing sodium sulfate; the precipitate must be continuously washed until a sample of the wash-water, acidified with hydrochloric acid, no longer gives a precipitate on the addition of barium chloride. As a rule, it is not advisable to run the wash-water into the filtrate, because this occasions an unnecessary dilution of the latter. The filter must always be smaller than the funnel, and the precipitate should not extend higher than to within 5 mm. of the top of the filter. Finally, large precipitates should be avoided as far as possible, for they render exact work more difficult — filtration and washing consuming too much time.

II. Reactions in the Dry Way

These reactions are employed chiefly in the so-called "preliminary examination," in testing the purity of precipitates, and in the examination of minerals. The most important reactions of this nature consist in the testing of a substance with regard to its —

1. Fusibility;
2. Ability to color the non-luminous Bunsen flame;
3. Volatility;
4. Behavior toward oxidation and reduction.

In order to carry out these reactions it is customary to use the non-luminous gas flame; and to understand the operations to be described it is necessary for us to know something about the composition of illuminating gas and the nature of the flame.

Illuminating gas, when made by the destructive distillation of coal, contains about 1.5 per cent CO_2, 4.0 per cent C_nH_{2n} compounds (illuminants), 0.4 per cent O_2, 8.5 per cent CO, 49.8 per cent H_2, 29.5 per cent CH_4, 3.2 per cent C_2H_6, and 3.2 per cent. N_2.

All these components, except CO_2, O_2 and N_2 (which are present only in small amounts), are combustible; they are reducing substances. Illuminating gas ordinarily burns with a luminous flame, and the luminosity is due to the presence of unsaturated hydrocarbons (C_nH_{2n}), principally ethylene, propylene, acetylene, etc. If ethylene is heated to a certain temperature, it is decomposed into methane and carbon:

$$C_2H_4 = CH_4 + C,$$

and it is glowing carbon which causes the luminosity of the flame.

The other unsaturated hydrocarbons behave like ethylene. The remaining combustible constituents of illuminating gas burn with a non-luminous flame. If we bring air into the gas, the flame becomes non-luminous. With the Bunsen burner air is introduced by opening the holes at the base of the burner. In such a gas-flame there are, according to Bunsen, the following parts (Fig. 1*):

I. *The inner cone* of the flame, *aab*, in which no combustion takes place, because the temperature here is too low. This part of the flame contains unburned gas mixed with about 62 per cent of air.

II. *The flame mantle*, indicated by *acaba*, which is composed of burning gas and air.

III. *The luminous tip*, at *b*, which does not appear unless the air-holes are closed somewhat.

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* In the drawing, the lines *d* represent a metallic chimney, or *flame-protector*, which rests upon the support *ee*. It is advisable to furnish each burner with such a flame protector.

In these three principal parts of the flame Bunsen distinguished six reaction zones:

1. *The base of the flame at α′.* The temperature here is relatively low, because the burning gas is cooled by the constant current of fresh air, and also because the burner itself conducts away considerable heat. This part of the flame serves to test volatile substances to see whether they impart color to the flame. In case several substances are present which color the flame, it is often possible to observe the colors one after the other, in that the most volatile substance colors the flame first, and later the colors caused by the less volatile ones are seen. This would not be possible at a hotter part of the flame, as all of the substances would then be immediately volatilized, producing a mixture of colors.

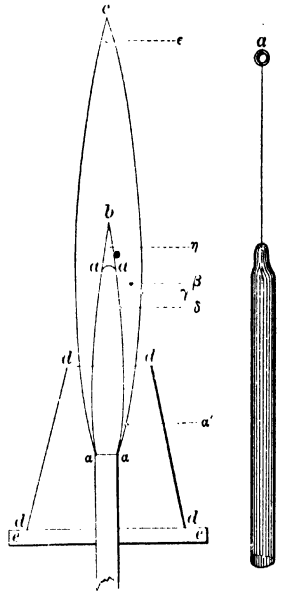

FIG. 1

2. *The fusing zone at β.* This lies at a distance of somewhat more than one-third of the height of the flame, and equidistant from the outside and the inside of the mantle, which is broadest at this part. As this is the hottest part of the flame, it serves for testing substances as to their fusibility and volatility.

3. *The lower oxidizing flame* lies in the outer border of the fusing zone at γ, and is especially suited for the oxidation of substances dissolved in vitreous fluxes.

4. *The upper oxidizing zone,* at ε, consists of the non-luminous tip of the flame, and acts most effectively when the air-holes of the lamp are fully open. It is used for various oxidizing tests, the roasting away of volatile products of oxidation, and generally for all processes of oxidation where the very highest temperature is not required.

5. *The lower reducing zone* lies at δ, in the inner border of the fusing zone next to the dark cone. As the reducing gases are mixed here with oxygen from the air, many substances which are reduced by the upper reducing flame are unaffected in this zone. This part of the flame is consequently very well adapted for a test which cannot be made

with the blowpipe, namely, reduction on the charcoal stick, and in vitreous fluxes.

6. *The upper reducing flame* is at η, in the luminous tip of the dark inner cone which may be produced by gradually diminishing the supply of air. If the luminous tip has been made too large, a test-tube or porcelain dish filled with water and placed over it will be blackened, which should never be the case. This luminous tip contains no free oxygen, is rich in separated incandescent carbon, and has, therefore, a much stronger reducing action than the lower reducing zone. It is used more particularly for the reduction of oxides collected in the form of incrustations.

Methods for the Examination of a Substance in the Dry Way

1. Test of the Fusibility

This test is principally made in the examination of minerals, which are introduced into the flame in the loop of a platinum wire (about as thick as a horsehair). The sample is examined, after heating, by means of a magnifying glass to see whether the corners are rounded, due to melting. The potentially hottest temperature of the fusing zone amounts to about 2300° C.* It will never be possible to reach this temperature with the test, because the substance itself loses heat by radiation. As the amount of heat lost by radiation is proportional to the surface exposed, it is evident that we will obtain the maximum heat by using a very small sample and holder. For this reason a coarse wire should not be used for this test.

We distinguish the following degrees of heat:

1. Faint red glow	525° C.	Melting-point of magnesium	631°
2. Dark red glow	700°	aluminium	658.7°†
3. Bright red glow	950°	silver	960.5°
4. Yellow glow	1100°	gold	1063°
		copper	1083°
5. Faint white glow	1300°	nickel	1452°
6. Full white glow	1500°	platinum	1755°

Below 525° C. the following substances melt: tin at 232°, bismuth at 271°, lead at 327°, zinc at 420°.

* This temperature will be considerably lower with too large a supply of air. According to Naumann, the temperature of illuminating gas with 1½ times its volume of air reaches about 1818° C., but the temperature obtained is usually much lower owing to loss by radiation. The finest platinum wire can be melted by means of the flame, but not when it is as thick as a horsehair.

† Circular No. 35 of the Bureau of Standards, Washington, D. C. Cf. Burgess-Le Chatelier: "High-Temperature Measurements."

2. Color Imparted to the Flame

The substance (best in the form of the chloride) is placed in the loop of a fine platinum wire, introduced into the base of the flame, and then finally brought into the fusing zone.

3. Test of the Volatility

A little of the substance is heated in a small test-tube or in a piece of glass tubing sealed at one end. Volatile substances are transformed into vapor, often without melting, and the vapors condense on the cooler walls of the tube.

4. Oxidation and Reductions

(a) *In Vitreous Fluxes or Beads*

To make a bead, borax ($Na_2B_4O_7 \cdot 10H_2O$) or salt of phosphorus ($NaNH_4HPO_4 + 4H_2O$) is used. A piece of very fine platinum wire, about 3 cm. long, is sealed into the end of a glass tube. The wire is heated to redness, and then quickly dipped into the borax or salt of phosphorus, held near the flame, whereby a small amount of the salt is fused to the end of the wire. By repeated heating and dipping into the salt a bead of sufficient size is obtained. This should be about 1.5 mm. in diameter at the most. It is not advisable to make a loop at the end of the wire, because in this way the exposed surface is unnecessarily increased. There is no danger of the bead falling off, provided the wire is held horizontally in the flame and the bead is not too large. In order to bring the substance in question into the bead, it is only necessary to moisten the latter with the tongue, and then dip it into the finely powdered substance, which will cause a small amount to adhere to the bead. It is preferable to introduce too little substance into the bead rather than too much, because, in the latter case, the bead will become dark and opaque. The oxidation of the substance in the bead is brought about by heating it in the lower oxidizing flame; reduction is usually effected by heating in the lower

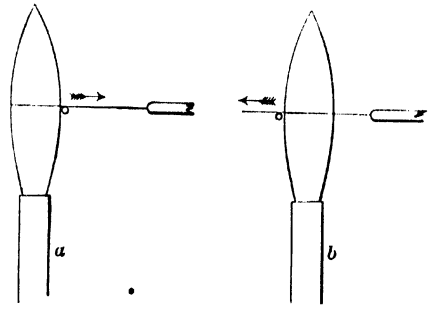

Fig. 2

reducing zone, and cooling in the dark inner cone, in order to prevent oxidation, which might take place if the substance were cooled in the air.

In order to clean the wire, a borax bead is produced on the wire, which is then heated, as is shown in Fig. 2, *a*, on one side of the bead only, so that the latter runs along the wire in the opposite direction, dissolving off all impurities. By heating the bead from the other side, Fig. 2, *b*, it is driven toward the end of the wire, from which it can be shaken off by a quick jerk. By repeating this process three times the wire is cleaned with the exception of a small amount of adhering borax-glass, which can be removed by heating the wire in the fusing zone until the sodium flame entirely disappears.

(*b*) *Reduction on the Charcoal Stick*

These exceedingly beautiful reactions are among the most sensitive of those used in analytical chemistry, and should be faithfully practiced by every beginner. The cause of their sensitiveness is due to their taking place on the extreme end of a tiny piece of charcoal, that is at *a point*, so that the sample has no opportunity to spread itself over a large surface, which is the case with the ordinary reactions on charcoal before the blowpipe.

To carry out these reactions, we use an ordinary splinter consisting of good, straight fibers, such as used in an old-fashioned brimstone match (not a safety-match, which has already been subject to chemical treatment). It is impregnated with sodium carbonate (soda) in the following manner: A crystal of sodium carbonate ($Na_2CO_3 \cdot 10\,H_2O$) is warmed in the flame, whereby it melts in a part of its water of crystallization. Three-fourths of the length of the match is now smeared with this liquid soda, and the match is then slowly rotated on its axis in the flame, until the soda melts and penetrates the charcoal. On withdrawal from the flame there should be no place which continues to glow; should the latter be the case, the stick should be quickly immersed in the soda again. In this way one obtains a solid little piece of charcoal, which can be heated for a long time without burning through.

In order to carry out a reduction, a small amount of the substance to be examined is mixed on the palm of the hand with an equal amount of anhydrous sodium carbonate, a small drop of melted sodium carbonate crystal is added, and the mixture is made into a paste by means of the blade of a penknife. The heated piece of charcoal is then rubbed into the mixture, which adheres to it. The sample is first heated in the lower oxidizing flame until it has melted, and then moved into the lower reducing flame. The reduction will be made

evident by a violent swelling up of the melt, caused by the evolution of carbon dioxide. As soon as the mass melts quietly the reduction is complete. The substance is allowed to cool in the dark cone, after which it is removed from the flame. The metal is now found on the extreme end of the carbonized match, concentrated in a point. This point is broken off, and triturated with a small amount of water in an agate mortar. The excess of sodium carbonate goes into solution, part of the charcoal floats on the surface of the water, while the heavier metal sinks to the bottom. In case the reduced metal is iron, nickel, or cobalt, it will not be noticeable to the eye, but it may be taken up with a magnetized knife-blade, to which it will adhere, usually mixed with charcoal. This should be dried by cautious warming, the tuft of metal taken off, rubbed between the thumb and forefinger, and then brought into contact with the knife again, to which only the metal will now adhere. The metal is then transferred to a piece of washed filter-paper about 3–4 mm. wide and 50 mm. long, so that it comes as near as possible to the end of the strip. By means of a capillary tube, a drop of hydrochloric acid and one of nitric acid are added, and the paper is warmed over the flame until the black speck (the metal) has disappeared, when the final test can be made.

In order to test for iron, a drop of potassium ferrocyanide is added, whereby the presence of iron is shown by the appearance of a distinct formation of Prussian blue. To test for nickel and cobalt, the metal is dissolved in nitric acid, the excess of acid is evaporated off, and a drop of concentrated hydrochloric acid added, whereby the paper is colored blue if cobalt is present; the nickel shows at the most only a very weak greenish color — usually, however, no color. A little caustic soda solution is now added, and the paper held in the vapors of bromine; in case either nickel or cobalt is present a brownish-black spot appears, due to the formation of either $Ni(OH)_3$ or $Co(OH)_3$.

If, however, the metal reduced was malleable, it is usually obtained in the form of a metallic globule on the end of the match, where it can be examined with the aid of a lens. Copper is not always obtained as a globule, but usually as a reddish, sintered mass. By pressing down on a malleable metal in the agate mortar it is obtained as a glistening fragment, which can be readily separated from the specifically lighter charcoal by washing. To accomplish this the agate mortar is inclined and a stream of water is directed sideways upon the mass, whereby the charcoal is washed out with the water, and the metal is left clean. It is transferred to a watch-glass and tested as follows:

1. *The Metal is White* (Pb, Sn, Ag, Pt). The metal is treated with a few drops of nitric acid and carefully warmed. Lead and silver

dissolve readily, particularly upon addition of a little water. Silver will be detected by the addition of a drop of hydrochloric acid, whereby white silver chloride, soluble in ammonia, is precipitated. The test for lead is dilute sulfuric acid, which precipitates white lead sulfate.

If the metal, on treatment with nitric acid, remains unchanged, it is probably platinum. It should be dissolved in aqua regia, evaporated to dryness, dissolved in a little water, and potassium chloride solution added. A yellow, crystalline precipitate confirms the presence of platinum. If the metal, when treated with nitric acid, becomes changed into a white insoluble oxide, it is tin. In this case, another fragment of metal is dissolved in concentrated hydrochloric acid and tested for tin by means of mercuric chloride solution, or by a solution of bismuth oxide in caustic soda.

2. *The Metal is Yellow to Red* (Cu, Au). Copper is readily dissolved in nitric acid, and the solution gives with potassium ferrocyanide a reddish-brown precipitate. Gold is insoluble in nitric acid, but soluble in aqua regia. The evaporated solution gives a violet-brown color with stannous chloride, due to finely divided gold.

(c) *Reduction in a Glass Tube*

Besides the borax bead and the charcoal stick, reduction is often effected by means of metallic sodium, potassium, or magnesium.

Thus small amounts of phosphorus in anhydrous salts may be detected in the following manner: The substance to be tested is placed in a glass tube, 3 mm. wide and 50 mm. long, which is closed at one end. A small cylinder of potassium or sodium (freed from petroleum by rubbing between filter-paper), or even a piece of magnesium wire, is added to the tube, and the contents then heated until the glass itself begins to soften. The reaction is so violent that the substance seems to take fire. After cooling, the tube is broken in a porcelain mortar, when by breathing over the mass, the smell of phosphoretted hydrogen may be detected.

The halogens, sulfur, and nitrogen are tested for in a similar way, as will be shown later.

(d) *Reduction in the Upper Reducing Flame for the Purpose of Forming Metallic and Oxide Incrustations*

The volatile elements which are reducible by means of hydrogen or charcoal may be detected in this part of the flame with the greatest ease, as, for example, arsenic, antimony, cadmium, bismuth, selenium, and tellurium. The metallic incrustations are obtained by holding in one hand a small portion of the substance on a thin asbestos thread

(platinum will be attacked) in the upper reducing zone of a small gas flame, where the oxide is reduced to volatile metal, and burned in the upper oxidizing flame to oxide. In the other hand, closely over the substance to be tested, is held a glazed porcelain evaporating-dish, filled with water, as is indicated in Fig. 3 at *B*. The metallic vapors are condensed by the cold dish, and deposited on it in the form of a metallic mirror or film. If, however, the dish is held above the upper oxidizing flame (at *A*), there is formed a thin, often invisible, oxide incrustation on the bottom.

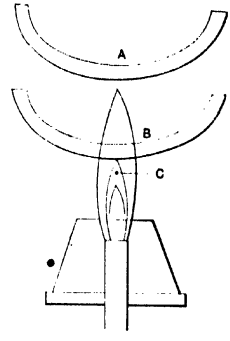

FIG. 3

Should it be necessary to treat the metallic incrustation with a large amount of solvent (as is necessary in the detection of selenium and tellurium), the porcelain dish is replaced by a test-tube half filled with cold water. A somewhat larger test-tube is used to hold the solvent, and the smaller test-tube, on which the incrustation was deposited, is placed within the larger tube and the liquid warmed if necessary.

(*e*) *Blowpipe Reduction on Charcoal*

These tests are made in the so-called "preliminary examination." For this purpose a small cavity is made with a penknife in a piece of good charcoal (preferably of linden wood), in which a knife-bladeful of the substance to be tested is placed, previously mixed with twice as much anhydrous sodium carbonate. As charcoal is a porous substance, it will readily absorb melted substances, such as a salt of the alkalies. Other substances are changed, by means of the sodium carbonate used, into carbonates, which are, for the most part, decomposed, on heating, into oxides and carbon dioxide. The oxides of the noble metals are decomposed, without the aid of the charcoal, into oxygen and metal; while those of the remaining metals are either reduced to metal or remain unchanged. Thus CuO, PbO, Bi_2O_3, Sb_2O_3, SnO_2, Fe_2O_3, NiO, and CoO are reduced either to a fused metallic globule (Pb, Bi, Sb, Sn, Ag, and Au), or to a sintered mass of metal (Cu), or to a glistening metallic fragment (Fe, Ni, Co, Pt). The oxides of zinc, cadmium, and arsenic do not give metallic globules, but are, however, easily reduced to metal. These metals are so volatile that they are changed into vapors, and are carried from the reducing zone of the flame into the oxidizing zone, where they are changed into difficultly

volatile oxides. These oxides, which have characteristic colors, are then deposited on the charcoal outside the cavity.

Zinc gives an incrustation which is yellow while hot, and white when cold; that of cadmium is brown; while the oxide of arsenic gives a white and readily volatile incrustation. Furthermore, the volatilization of arsenic gives rise to a characteristic garlic odor. The metals lead, bismuth, and tin give, besides the metallic globule, an oxide incrustation which is typical.

At the same time, nitrates, nitrites, chlorates, etc., may be recognized by the fact that they cause a very rapid combustion of the glowing charcoal (deflagration). This deflagration is not to be confused with a decrepitation which takes place on heating substances containing enclosed moisture or gases, such as rock salt, fluor-spar, etc. Crystals of such substances are burst by the quick expansion of the enclosed liquid, and scattered about.

Many difficultly fusible substances do not melt into the charcoal. Thus many silicates form a bead with the soda, which only after *continuous* heating will give up the alkali and allow it to be absorbed by the charcoal, leaving behind the white infusible silica. Phosphates and borates act similarly, only these do not leave behind an oxide, but a fused glass. Infusible white oxides, as those of calcium, strontium, magnesium, aluminium, and many of the rare earths (Welsbach mantle, for example), glow very brightly, and in fact more brightly as they are more strongly heated.

Division of the Metals into Groups

The metals, for purposes of analytical chemistry, may be divided into five groups:

The *First Group* contains those metals whose *chlorides are insoluble*, or difficultly soluble, and whose sulfides are insoluble in dilute acids. They may, therefore, be precipitated from their solutions by means of either hydrochloric acid or hydrogen sulfide

The *Second Group* contains those metals whose chlorides are soluble, but whose *sulfides are insoluble* in dilute acids. They may be precipitated from their solutions by means of hydrogen sulfide, but not by hydrochloric acid.

The *Third Group* contains those metals whose *sulfides are soluble in dilute acids*, but are insoluble in water and alkalies; and also those metals whose sulfides are hydrolytically decomposed into hydrogen sulfide and insoluble hydroxide. The members of this group are precipitated completely by *hydrogen sulfide only from alkaline solutions*.

The *Fourth Group* contains those metals whose sulfides are soluble

in water, but whose *carbonates are insoluble in the presence of ammonium chloride.* They are precipitated by *ammonium carbonate* in the presence of ammonium chloride, but not by any of the above reagents.

The *Fifth Group* contains magnesium and the alkalies; they are not precipitated by any of the above reagents.

This purely arbitrary grouping is based upon certain specific solubilities and does not classify the general chemical behavior of the elements as the periodic system of grouping does. In some cases the members of the analytical group all belong to the same group in the periodic system but this is not usually true. In the following table which shows how the elements are grouped according to the periodic system, the analytical group to which each metal belongs is shown by a Roman numeral placed in the upper right-hand corner of the space in which the symbol of the element is given.

PERIODIC GROUPING OF THE ELEMENTS

O	I	II	III	IV	V	VI	VII	VIII		
				RH_4	RH_3	RH_2	RH			
R	R_2O	RO	R_2O_3	RO_2	R_2O_5	RO_3	R_2O_7	RO_4, RO_3, RO_2, R_2O_3		
	H 1.008									
He 4.0	V Li 6.94	Gl 9.1	B 10.9	C 12.005	N 14.008	O 16.00	F 19.0			
Ne 20.2	V Na 23.00	IV or V Mg 24.32	III Al 27.1	Si 28.3	P 31.04	S 32.06	Cl 35.46			
Ar 39.9	V K 39.10	IV Ca 40.07	Sc 45.1	III Ti 48.1	III V 51.0	III Cr 52.0	Mn 54.93	Fe 55.84	Co 58.97	Ni 58.68
	II Cu 63.57	III Zn 65.37	Ga 70.1	III Ge 72.5	II As 74.96	II Se 79.2	Br 79.92			
Kr 82.92	V Rb 85.45	IV Sr 87.63	Yt 89.33	III Zr 90.6	III Nb 93.5	III Mo 96.0		Ru 101.7	Rh 102.9	Pd 106.7
	I Ag 107.88	II Cd 112.4	In 114.8	II Sn 118.7	II Sb 120.2	II Te 127.5	I 126.92			
Xe 130.2	V Cs 132.81	IV Ba 137.37	La 139.0	* III Ce 140.25	III Ta 181.5	II W 184.0		Os 190.9	Ir 193.1	Pt 195.2
	II Au 197.2	I & II Hg 200.6	II Tl 204.0	I & II Pb 207.2	II Bi 208.0					
		IV Ra 226.0		III Th 232.15		III U 238.2				

* Twelve other " rare earths " with atomic weights ranging from 140.6 to 175.0 belong here. They all belong to the same group in qualitative analysis.

In order to carry out an analysis with certainty it is necessary to understand not only the reactions of the different elements, but also the *sensitiveness* of each reaction. The analyst should be able to draw a conclusion by the size of the precipitate formed as to the approximate amount which is present in the original substance. This, however, is possible only when the experiments are made with known amounts. *Consequently reagents of a known strength are used and allowed to act on known amounts of the different substances.* According to the suggestion of R. Blochmann * it is well to make the solutions of the different reagents either double-normal, normal, half-normal, or tenth-normal. For many years the author has used in his laboratory solutions of reagents and salts according to this principle, and has found that the beginner in this way gets a far better understanding of the stoichiometrical relations than when solutions of almost any concentration are used, as was formerly the custom.

By a *normal* solution is understood one which contains in a liter one gram-equivalent of the substance in question, referred to a gram-atom of hydrogen as a unit. A tenth-normal solution will contain one-tenth of a gram-equivalent in a liter, etc.

Thus one liter of a normal solution will contain

HCl	$= 36.47$ gms.	
$\frac{H_2SO_4}{2}$	$= \frac{98.08}{2} = 49.04$ gms.	
$\frac{H_3PO_4}{3}$	$= \frac{98.06}{3} = 32.69$ gms.	equivalent to one gram-atom of hydrogen.
$NaOH$	$= 40.01$ gms.	
$\frac{KMnO_4}{5}$	$= \frac{158.03}{5} = 31.61$ gms.†	
$\frac{K_2Cr_2O_7}{6}$	$= \frac{294.2}{6} = 49.03$ gms.‡	

The great advantage of this system is that one always knows how much of one solution should be used in order to react with another quantitatively. Thus 1 cc. of a normal caustic soda solution will

* *Berichte*, **1890**, 31.

† This is considering the solution as an oxidizing agent. As a precipitant, the normal solution of $KMnO_4$ would contain one mole per liter. The reagent is almost invariably used as an oxidizing agent and not as a precipitant.

‡ Also considered as an oxidizing agent. As a precipitant, the normal solution of $K_2Cr_2O_7$ used to form $PbCrO_4$ or $BaCrO_4$ would contain one-fourth mole per liter.

neutralize 1 cc. of any normal acid, or 2 cc. of any half-normal acid. In the same way 1 cc. of a normal solution of sulfuric acid, or of any sulfate, will precipitate quantitatively the barium from 1 cc. of a normal barium chloride solution.

The Laboratory Reagents

I. Concentrated Acids

	Sp. gr.	Per cent by Wt.	Approx. Conc.
Hydrochloric acid	1.19	37.9	12 N.
Hydrofluoric acid	.....	.....	24 N.
Nitric acid	1.42	69.8	16 N.
Phosphoric acid	1.7	85.0	15 N.
Sulfuric acid	1.84	96.0	36 N.

II. Diluted Acids

	Sp. gr.	Per cent by Wt.	Approx. Conc.
Acetic acid	1.047	35.0	6 N.
Hydrochloric acid	1.10	20.0	6 N.
Nitric acid	1.20	32.3	6 N.
Perchloric acid	1.12	.....	2 N.
Sulfuric acid	1.18	24.8	6 N.
Sulfurous acid	(Satd. soln. of SO_2)		0.33 N.
Tartaric acid	(150 g. per liter)		2 N.

III. Bases

	Sp. gr.	Per cent by Wt.	Approx. Conc.
Ammonium hydroxide	0.90	28% NH_3	15 N.
Ammonium hydroxide	0.96	9.9% NH_3	6 N.
Barium hydroxide	(satd. soln. $Ba(OH)_2 \cdot 8H_2O$)		0.4 N.
Potassium hydroxide	1.37	36.9	9 N.
Sodium hydroxide	1.22	19.7	6 N.

IV. Salts

(a) *Ammonium Salts*

Name of Salt.	Directions for Making Reagent.	Conc.
Ammonium acetate $NH_4C_2H_3O_2$ or NH_4Ac	Mix equal volumes of 6-normal acetic acid and 6-normal ammonia.	3 N.
Ammonium carbonate $(NH_4)_2CO_3$	Dissolve 250 gms. freshly powdered ammonium carbonate in 1 liter 6-normal NH_4OH. The commercial salt is $NH_4HCO_3 \cdot NH_4CO_2NH_2$.	6 N.
Ammonium chloride NH_4Cl	Dissolve 54 g. in 1 liter of water.	N.
Ammonium molybdate $(NH_4)_2MoO_4$	Dissolve 90 g. of pure ammonium molybdate in 100 cc. of 6-normal NH_4OH, add 240 g. of NH_4NO_3 and dilute to 1 liter. The formula of the commercial salt is $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$.	N. (3 N. in NH_4NO_3)
Ammonium oxalate $(NH_4)_2C_2O_4$	Dissolve 35 g. $(NH_4)_2C_2O_4 \cdot H_2O$ in 1000 cc. water.	0.5 N.
Ammonium polysulfide $(NH_4)_2Sx$	Digest 1 liter 6-normal ammonium monosulfide with 25 gms. flowers of sulfur for some hours and filter.	6 N.
Ammonium sulfide $(NH_4)_2S$	Pass H_2S into 200 cc. 15-normal NH_4OH in a bottle immersed in running water or in ice water until no more gas is absorbed; then add 200 cc. 15-normal NH_4OH and dilute to 1 liter.	6 N.

(*b*) *Other Salts*

Name of Salt.	Formula.	Formula Weight.	Grams per Liter.	Conc.
Alum	$KAl(SO_4)_2 \cdot 12H_2O$	475	59	0.5 N.
Barium chloride	$BaCl_2 \cdot 2H_2O$	244	122	N.
Bismuth nitrate	$Bi(NO_3)_3 \cdot 5H_2O$	484	80	0.5 N.
Cadmium nitrate	$Cd(NO_3)_2 \cdot 4H_2O$	308	154	N.
Cadmium sulfate	$3CdSO_4 \cdot 8H_2O$	770	64	0.5 N.
Calcium chloride	$CaCl_2 \cdot 6H_2O$	219	110	N.§
Calcium sulfate	$CaSO_4 \cdot 2H_2O$	172	2.6	Satd.
Chrome-alum	$KCr(SO_4)_2 \cdot 12H_2O$	499	62	0.5 N.
Cobalt nitrate	$Co(NO_3)_2 \cdot 6H_2O$	291	50	1% Co
Copper sulfate	$CuSO_4 \cdot 5H_2O$	250	125	N.
Ferric chloride	$FeCl_3 \cdot 6H_2O$	270	90	N.*
Ferric nitrate	$Fe(NO_3)_3 \cdot 9H_2O$	404	135	N.
Lead acetate	$Pb(C_2H_3O_2)_2 \cdot 3H_2O$	379	190	N.
Magnesium sulfate	$MgSO_4 \cdot 7H_2O$	247	123	N.
Manganese sulfate	$MnSO_4 \cdot 4H_2O$	223	56	0.5 N.
Mercuric chloride	$HgCl_2$	272	27	0.2 N.
Mercurous nitrate	$Hg_2(NO_3)_2 \cdot 2H_2O$	561	280	N.
Nickel sulfate	$NiSO_4 \cdot 7H_2O$	281	70	0.5 N.
Potassium bichromate	$K_2Cr_2O_7$	294	49	N.†
Potassium chromate	K_2CrO_4	194	291	3 N.*
Potassium cyanide	KCN	65	65	N.
Potassium ferricyanide	$K_3[Fe(CN)_6]$	329	110	N.*
Potassium ferrocyanide	$K_4[Fe(CN)_6] \cdot 3H_2O$	422	105	N.*
Potassium iodide	KI	166	17	0.1 N.
Potassium nitrite	KNO_2	85	255	3 N.
Potassium oxalate	$K_2C_2O_4 \cdot H_2O$	184	276	3 N.
Potassium permanganate	$KMnO_4$	158	10	0.3 N.†
Potassium thiocyanate	KCNS	97	97	N.
Silver nitrate	$AgNO_3$	170	17	0.1 N.
Sodium acetate	$NaC_2H_3O_2 \cdot 3H_2O$	136	136	N.
Sodium arsenite	$NaAsO_2$	130	130	N.
Sodium bromide	$NaBr \cdot 2H_2O$ or NaBr	139 or 103	69 or 51	0.5 N.
Sodium carbonate	Na_2CO_3	106	159	3 N.
Sodium hypochlorite	NaClO	74	37	N.†
Sodium nitrite	$NaNO_2$	69	207	3 N.‖
Sodium phosphate	$Na_2HPO_4 \cdot 12H_2O$	358	119	N.
Sodium sulfate	$Na_2SO_4 \cdot 10H_2O$	322	160	N.
Sodium thiosulfate	$Na_2S_2O_3 \cdot 5H_2O$	248	124	0.5 N.‡
Uranyl acetate	$UO_2(C_2H_3O_2)_2 \cdot 2H_2O$	424	21	0.1 N.

V. Special Reagents

Chloroplatinic acid: Dissolve 26.5 gms. $H_2[PtCl_6] \cdot 6\ H_2O$ (corresponding to 10 gms. Pt) in 100 cc. water.

Ether saturated with HCl: Saturate anhydrous ether at 0° with dry HCl gas.

Dimethylglyoxime: Dissolve 12 g. of the solid in 1 liter of 95 per cent ethyl alcohol.

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* As precipitant. † As oxidizing agent. ‡ As reducing agent.

§ This reagent must be free from sulfate.

‖ In case the salt contains chloride mix with 1 per cent of its volume of silver nitrate and filter after shaking. Note on the label that the reagent contains $AgNO_3$.

Ferrous sulfate, 2 N: Dissolve 280 gms. $FeSO_4 \cdot 7H_2O$ in 6 N sulfuric acid and keep in contact with iron nails.

Hydrogen peroxide, 3 per cent.

Magnesium ammonium chloride, N in $MgCl_2$: Dissolve 100 gms. $MgCl_2 \cdot 6H_2O$ and 100 gms. NH_4Cl in water, add 50 cc. 15-normal NH_4OH and dilute to 1 liter.

Magnesium ammonium nitrate, 1-normal in $Mg(NO_3)_2$, 3-normal in ammonium nitrate. Dissolve 130 g. of $Mg(NO_3)_2 \cdot 6H_2O$ and 240 g. NH_4NO_3 in water, add 35 cc. of 6-normal NH_4NO_3 and dilute to 1 liter.

Potassium mercuric iodide, 0.5 normal in K_2HgI_4: Dissolve 115 gms. HgI_2 and 80 gms. KI in enough water to make the volume 500 cc.; add 500 cc. 6-normal NaOH and decant the solution from any precipitate that may form on standing. The stock solution should be kept in the dark. For sensitive work the water used, as well as the solids, must be absolutely free from ammonia.

Potassium pyroantimonate: Add 22 gms. of the best commercial salt to 1 liter of boiling water, boil until nearly all the salt has dissolved, cool quickly, add 35 cc. of 10 per cent KOH solution, and filter after standing over night.

Sodium cobaltinitrite: Dissolve 230 gms. $NaNO_2$ in 500 cc. water, add 155 cc. 6-normal $HC_2H_3O_2$ and 30 gms. $Co(NO_3)_2 \cdot 6H_2O$. Let the mixture stand over night, filter and dilute to 1 liter.

Sodium sulfide, 3-normal in Na_2S, 1-normal in Na_2S_2 and 1-normal in NaOH. Dissolve 480 g. of $Na_2S \cdot 9H_2O$ and 40 g. of NaOH in water, add 16 g. of sulfur shake until the S is all dissolved and dilute to 1 liter.

Stannous chloride, 1-normal: Dissolve 115 gms. $SnCl_2 \cdot 2H_2O$ in 170 cc. 12-normal, HCl, dilute to 1 liter and keep in bottles containing a strip of pure tin.

Starch and potassium iodide: Rub 20 gms. soluble starch to a thin paste with a little water in a mortar and pour the paste into 1 liter of boiling water. Boil five minutes and filter through a loose plug of cotton wool. Add 10 gms. KI and 5 cc. chloroform to the filtrate.

Thiourea: Dissolve 100 g. of the solid in 1 liter of water.

Turmeric: Shake turmeric powder with 95 per cent alcohol and filter.

Urea: Dissolve 200 gms. urea in 1 liter 6-normal HCl.

VI. Saturated Solutions

	1000 cc. water dissolves
Barium hydroxide	68 gms. $Ba(OH)_2$ at 20°
Bromine water	32.68 gms. Br_2
Calcium sulfate	2.6 gms. $CaSO_4 \cdot 2H_2O$
Chlorine water	6.5 gms. Cl_2
Hydrogen sulfide	4.2 gms. H_2S
Lime water	1.3 gms. CaO
Sulfurous acid	106 gms. SO_2

VII. Special Solvents

Amyl alcohol	Chloroform
Carbon disulfide	Ethyl alcohol (95 per cent)
Carbon tetrachloride	Methyl alcohol (free from acetone)

VIII. Solid Reagents

Absorbent cotton
Aluminium turnings
Ammonium chloride, NH_4Cl
Ammonium nitrate, NH_4NO_3
Barium carbonate, $BaCO_3$
Bismuth dioxide, may be used in place of sodium bismuthate
Borax, $Na_2B_4O_7\ 10\ H_2O$
Boric acid, H_3BO_3
Calcium chloride (anhydrous)
Calcium oxide
Calcium phosphate
Chloride of lime, $CaOCl \cdot Cl$
Copper wire or turnings
Ferrous sulfate, $FeSO_4 \cdot 7\ H_2O$
Ferrous sulfide, FeS
Iron nails, Fe
Iron powder
Lead (finely granulated) Pb
Lead dioxide (free from Mn), PbO_2
Litmus paper, blue
Litmus paper, red
Paraffin
Potassium acid sulfate (fused), $KHSO_4$
Potassium carbonate, K_2CO_3
Potassium chlorate, $KClO_3$
Potassium dichromate, $K_2Cr_2O_7$
Potassium ferricyanide, $K_3Fe(CN)_6$
Potassium iodide, KI
Potassium nitrate, KNO_3
Quartz powder
Silica (precipitated), SiO_2
Silver carbonate
Silver sulfate, Ag_2SO_4
Sodium acetate, $NaC_2H_3O_2$
Sodium ammonium phosphate (microcosmic salt), $NaNH_4HPO_4 \cdot 4\ H_2O$
Sodium bismuthate, $NaBiO_3$
Sodium carbonate, Na_2CO_3
Sodium peroxide, Na_2O_2
Sodium nitroprussiate, $Na_2[Fe(CN)_5] \cdot NO \cdot 2\ H_2O$
Sodium sulfide, $Na_2S \cdot 9\ H_2O$
Sodium tetraborate (see Borax)
Starch, $(C_6H_{10}O_5)_x$
Tartaric acid, $H_2C_4H_4O_6$
Tin (mossy)
Zinc (finely granulated)

Determination of the Sensitiveness of Reactions

The more sensitive a reaction is, the smaller will be the amount of the substance which can be detected in a given volume, in a definite time, with the reagent in question. Let us assume that the amount of substance taken is dissolved in 100 cc. of liquid, the time allowed to be two or three minutes, and the limit of sensitiveness to be the smallest amount of substance which can be detected under these conditions.

A few examples will make the method clear:

Magnesium salts are precipitated by means of sodium phosphate, in the presence of ammonium chloride and ammonia, in the form of magnesium ammonium phosphate. What is the sensitiveness of this reaction? We take 1 cc. of our normal magnesium sulfate solution, add three drops of ammonium chloride solution, and two or three drops of ammonia and sodium phosphate solutions; the characteristic white precipitate is formed immediately. We dilute, now, the normal solution of magnesium sulphate ten times, and repeat the experiment with 1 cc. of the diluted solution. The result will be —

1 cc. of	N.	Mg	solution,	100 cc.	= 1.2	g.	Mg,	reacts immediately.
1 cc.	N/10	Mg	"	100 cc.	= 0.12	"	Mg,	" "
1 cc.	N/100	Mg	"	100 cc.	= 0.012	"	Mg,	" "
1 cc	N/1000	Mg	"	100 cc.	= 0.0012	"	Mg,	" after a few seconds
1 cc.	N/10000	Mg	"	100 cc.	= 0.00012	"	Mg,	" after one or two minutes

If, therefore, 100 cc. of a solution contain 0.00012 gm. Mg, the magnesium can be detected within one or two minutes. Should the detection of smaller amounts be desired, the solution must be concentrated by evaporation.

This reaction can be called very sensitive. The following potassium reactions are much less delicate:

(*a*) *Reaction with Chloroplatinic Acid* (page 82)

1 cc. of 0.2 N KCl solution, 100 cc. = 0.78 gm. K, reacts with a drop of H_2PtCl_6 immediately.

1 cc. of 0.02 N KCl solution, 100 cc. = 0.078 gm. K, does not cause precipitation within three minutes.

1 cc. of 0.04 N KCl solution, 100 cc. = 0.156 gm. K, does not cause precipitation within three minutes; but does, however, on addition of two drops of alcohol.

1 cc. of 0.06 N KCl solution, 100 cc. = 0.234 gm. K, reacts immediately on stirring.

The sensitiveness of the reaction lies, therefore, between 0.156 and 0.234 gm. K per 100 cc. In order to detect smaller amounts of potassium than 0.156–0.234 gm. per 100 cc., the solution must be concentrated by evaporation.

(*b*) *Reaction with Tartaric Acid* (page 83)

1 cc. of 0.2 N KCl solution, 100 cc. = 0.78 gm. K, reacts immediately with two drops of sodium acetate and two drops of a concentrated solution of tartaric acid.

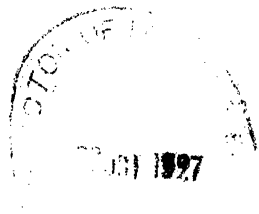
1 cc. of 0.02 N KCl solution, 100 cc. = 0.078 gm. K, reacts after one to two minutes with vigorous shaking.

This can be taken as the limit of sensitiveness.

If the beginner will test the delicacy of reactions in this way, he will quickly get a clear insight into the solubility relations of the different salts.

Probably the quickest way of learning these relations is to analyze first of all solutions known to contain an equal quantity of each constituent of a given group. It is well for the beginner to start with 100 cc. of solution and 0.02 gram of each dissolved cation or anion.

When the sensitiveness of the reactions is known, qualitative *tests are often the most accurate methods for estimating small quantities of substances.* Thus it is possible to detect very small quantities of titanium by means of the hydrogen peroxide test, and the most accurate method for determining such small quantities is to compare the intensity of the color change with that produced in a series of solutions containing known quantities of titanium.



PART II. REACTIONS OF THE METALS (CATIONS)

The separation of the metals into groups (cf. p. 70) is based upon the varying solubilities of the chlorides, sulfides, hydroxides and carbonates. In general, the metals removed first in the scheme of analysis are those which form the smallest number of soluble salts and the metals tested for last are those which form the largest number of soluble salts. In qualitative analysis, the relatively insoluble salts are of chief interest and it is, therefore, simplest to begin the study of the subject with that group of metals which is tested for last. Compounds containing these metals are very common and are used to some extent in the separation and identification of the metals of the other groups. A knowledge of the characteristic reactions of such compounds is necessary in order to understand the chemistry involved in the analysis of the other groups, and this furnishes another important reason for taking up the study in the reverse order to that in which the analysis is usually carried out. In this part of the book only the reactions of the more common elements will be considered. The rare elements, such as lithium, cesium and rubidium of the alkali group, will be considered in Part V.

GROUP V. THE ALKALI GROUP

POTASSIUM, K; SODIUM, Na; and AMMONIUM, NH_4

The metals potassium and sodium are the most reactive of all the common positive elements (cf. p. 41). They oxidize very rapidly when exposed to the air and decompose water at ordinary temperatures; the hydrogen of water is reduced to the gaseous condition and the metal is oxidized to alkali hydroxide in equilibrium with alkali cations and hydroxyl anions. On account of the extent of the ionization (cf. p. 10) the alkali hydroxides form very strong bases. The solid hydroxides are the most stable of all hydroxides; they do not break down into oxide and water even on being melted. The pure oxides are difficult to prepare; cautious heating of the metals in air results in the formation of considerable peroxide as well as oxide.

Ammonium is classed with the alkali metals because the solubility of ammonium salts is similar to that of potassium salts. The ammo-

nium radical differs from the alkali metals in being capable of oxidation, the usual product of the oxidation being nitrogen gas. Ammonium hydroxide is a much weaker base than the other hydroxides, and the salts are either volatile or are decomposed on being heated. The salts of potassium, sodium and ammonium are colorless for the most part, and readily soluble in water. Of these salts the carbonates, the tertiary and secondary phosphates, the cyanides, and the borates react alkaline in aqueous solution (hydrolysis). The salts of the alkalies are more or less volatile and impart to the non-luminous flame characteristic colors. When a solid is involved, either as initial substance or as final product, in any of the characteristic reactions of this and the following groups, it will be designated usually by bold-faced type in the equation. The formation of a gas will usually be indicated by placing an arrow after the symbol in an equation.

POTASSIUM, K. At. Wt. 39.10

Sp. Gr. 0.87. M. Pt. (Melting-point) 62.5° C.

Occurrence. — Sylvite (KCl), isometric, and carnallite ($MgCl_2 . KCl \cdot 6H_2O$) orthorhombic, occur at Stassfurt in the presence of halite and anhydrite. Saltpetre (KNO_3), orthorhombic prisms. Further, in very many silicates, e.g., monoclinic feldspar ($KAlSi_3O_8$), and muscovite ($KH_2Al_3Si_3O_{12}$); also in plants in the form of organic salts, which yield on combustion potassium carbonate (potash).

Reactions in the Wet Way

Potassium forms very few salts that are difficultly soluble in water. The chloroplatinate, acid tartrate, cobaltinitrite, and perchlorate are the least soluble, and are consequently used in the detection of potassium.

1. **Chloroplatinic Acid,*** $H_2[PtCl_6]$, gives in concentrated solutions of the chloride a yellow precipitate of potassium chloroplatinate,

$$PtCl_6^{--} + 2\,K^+ \rightarrow \mathbf{K_2[PtCl_6]},$$

which consists of small regular octahedra (visible with a magnifying-glass). In case the potassium solution is not very concentrated, no precipitation may appear at first; but on rubbing the inside of the beaker or test-tube with a glass rod the formation of the precipitate will be hastened.

* Platinic chloride, $PtCl_4$, gives no precipitate with potassium salts, or at least only after long standing. The above reagent, chloroplatinic acid, is a dibasic acid and is obtained by dissolving platinum in aqua regia. The solution is prepared of such strength that there are 10 gms. of platinum in every 100 cc.

This is always the case when a crystalline precipitate is formed. The solution is supersaturated before the precipitate separates out, and the formation of crystals is hastened by the formation of small scratches on the sides of the beaker.

The behavior of the potassium chloroplatinate on ignition is characteristic; it is decomposed into chlorine, platinum, and potassium chloride:

$$K_2[PtCl_6] = 2\,KCl + Pt + 2\,Cl_2\uparrow.$$

If the products of ignition are treated with water, and the platinum filtered off, the filtrate will again give with chloroplatinic acid the yellow crystalline precipitate of $K_2[PtCl_6]$. (Note difference from ammonium chloroplatinate.)

Solubility of the Potassium Chloroplatinate in Water.

100 cc. of water dissolve at 0°, 0.70 gm.; 10°, 0.90 gm.; 20°, 1.12 gms.; and at 100°, 5.18 gms. $K_2[PtCl_6]$.

In a saturated KCl solution, or in 75 per cent alcohol, the precipitate is practically insoluble.

For this reaction it is best to use the chloride. The addition of chloroplatinic acid to potassium iodide solution causes a deep-reddish-brown color due to the conversion of $[PtCl_6]^{--}$ into $[PtI_6]^{--}$ ion, of which the potassium salt is more soluble:

$$[PtCl_6]^{--} + 6\,I^- \rightarrow [PtI_6]^{--} + 6\,Cl^-.$$

Similarly, potassium cyanide is not precipitated by chloroplatinic acid, owing to the formation of complex platinum-cyanogen compounds.

To test an iodide or cyanide for potassium, the salt should first be changed to chloride by evaporation with concentrated hydrochloric acid.

2. **Tartaric Acid,** $H_2C_4H_4O_6$, produces, in not too dilute neutral solutions of potassium salts, a white crystalline precipitate of potassium acid tartrate (orthorhombic, hemihedral):

$$K^+ + H_2C_4H_4O_6 \rightarrow KHC_4H_4O_6 + H^+.$$

Rubbing the inside walls of the dish will hasten the formation of the precipitate.

Potassium acid tartrate is readily soluble in mineral acids, but difficultly soluble in acetic acid and water; 100 cc. of water at 10° C. dissolve 0.425 gm. of this salt. If sodium acetate is added to the solution, the hydrogen ions set free by the above reaction will unite with the acetate ions to form non-ionized acetic acid (cf. p. 47):

$$H^+ + C_2H_3O_2^- \rightarrow HC_2H_3O_2,$$

whereby the reaction is made much more sensitive. Too much sodium acetate, however, exerts a solvent action upon the potassium acid tartrate. In the presence of considerable sodium acetate, acetic acid is ionized to such a slight extent that the hydrogen ions from $HC_4H_4O_6$ disappear and, as a result, the potassium acid tartrate dissolves. Neutralization with caustic alkali is even less satisfactory; soluble alkali tartrate is formed:

$$KHC_4H_4O_6 + OH^- \rightarrow K^+ + C_4H_4O_6^{--} + H_2O.$$

On igniting potassium acid tartrate, empyreumatic vapors (smelling like burnt sugar) are given off and a mixture of carbon and potassium carbonate is left behind. If the mass is now moistened with hydrochloric acid, it will froth strongly. This behavior is characteristic not only of potassium tartrate, but is common to *all alkali salts of organic acids*. On ignition they are changed into carbonates, and when the acid is non-volatile, carbonization takes place; but with volatile acids there is at the most only a slight carbonization. With many metals the carbonate is not left unchanged; frequently it is broken up into carbon dioxide and oxide of the metal; in the case of salts of organic acids with reducible metals, the metal itself is left with the carbon. Thus sodium acetate will yield sodium carbonate and acetone, with only a slight carbonization:

$$2\,CH_3CO \cdot ONa = Na_2CO_3 + CH_3COCH_3.$$

Acetone (colorless volatile liquid, burns with luminous flame)

On gentle ignition, calcium oxalate yields calcium carbonate and carbon monoxide; the latter burns with a blue flame.

$$CaC_2O_4 = CaCO_3 + CO\uparrow.$$

On strong ignition, the calcium carbonate is decomposed into calcium oxide and carbon dioxide:

$$CaCO_3 \rightarrow CaO + CO_2\uparrow.$$

Tartrates of lead, iron, and many other metals on being ignited yield carbon and metal.

3. **Bismuth-Sodium Thiosulphate** (Carnot's * reaction). — If one drop of half-normal bismuth nitrate solution is mixed with two or three drops of half-normal thiosulfate solution and 10–15 cc. of absolute alcohol (any turbidity being removed by the careful addition of a very little water), a sensitive reagent for potassium ions is prepared in which the bismuth is present in a complex anion:

$$Bi^{+++} + 3\,S_2O_3^{--} \rightarrow Bi(S_2O_3)_3^-$$

* *Z. anal. Chem.* (1897), 512.

The sodium salt is soluble in alcohol but the yellow potassium salt is not:

$$Bi(S_2O_3)_3^{---} + 3\,K^+ \rightarrow \mathbf{K_3[Bi(S_2O_3)_3]}.$$

The presence of ammonium chloride prevents the reaction.

4. **Fluosilicic Acid,** H_2SiF_6, added in considerable excess to a solution of a potassium salt, precipitates gelatinous potassium fluosilicate,

$$SiF_6^{--} + 2\,K^+ \rightarrow \mathbf{K_2SiF_6},$$

which is difficultly soluble in water and dilute acids and insoluble in alcohol. On heating, it is decomposed into volatile silicon fluoride, and potassium fluoride remains behind:

$$\mathbf{K_2SiF_6} = \mathbf{2\,KF} + SiF_4\uparrow.$$

The solution must not be alkaline; the fluosilicate ion decomposes and silicic acid precipitates:

$$[SiF_6]^{--} + 4\,OH^- \rightarrow \mathbf{Si(OH)_4} + 6\,F^-.$$

5. **Perchloric Acid,** $HClO_4$, precipitates white, crystalline potassium perchlorate,

$$HClO_4 + K^+ \rightarrow H^+ + \mathbf{KClO_4};$$

100 cc. of water at 0° dissolve 0.07 gm., and at 100° 19.8 gms. $KClO_4$. It is so slightly soluble in 97 per cent alcohol that the precipitate can be obtained with less than 2 mgs. of potassium ions.

A dangerous explosion is likely to result if the alcoholic solution is heated.

6. **Sodium Cobaltinitrite,** $Na_3[Co(NO_2)_6]$, precipitates yellow potassium-sodium cobaltinitrite from neutral or slightly acid solution:

$$Na_3[Co(NO_2)_6] + 2\,KCl = \mathbf{K_2Na[Co(NO_2)_6]} + 2\,NaCl.$$

Ammonium salts give a similar precipitate, but moderate amounts of alkaline-earth elements or of lithium and sodium do not interfere. The test must not be made in alkaline solution or $Co(OH)_3$ will be precipitated. The reagent, prepared according to the directions on p. 77, permits the detection of 0.3 mg. of potassium within ten minutes. If the reagent is prepared according to the following directions of Biilmann,* as little as 0.0009 mg. potassium can be detected in the presence of 4000 equivalents of sodium.

7. The reagents used in testing for alkaloids, — picric acid or sodium picrate, sodium phospho-tungstate, and phospho-molybdic acid, give precipitates with potassium salts. With picric acid and phospho-molybdic acid the precipitates are yellow, but the precipitate produced by phospho-tungstic acid is white.

* *Z. anal. Chem.*, **39** (1900), 284

PREPARATION OF SODIUM COBALTINITRITE

Dissolve 150 gms. of sodium nitrite in 150 cc. of hot water and allow the solution to cool to about 40°, which will cause the deposition of some sodium nitrite crystals. Add 50 gms. of cobalt nitrate crystals, stir rapidly and add 50 cc. of 50 per cent acetic acid in small portions; stopper the flask and shake vigorously. Pass a rapid stream of air through the liquid and then allow it to stand quietly over night. In the morning, more or less brown precipitate will be found on the bottom of the flask due to a little potassium salt present in the sodium nitrite. Siphon off the clear liquid through a filter and add to the filtrate, while stirring, about 200 cc. of alcohol in small portions; this causes the precipitation of the greater part of the dissolved sodium cobaltinitrite. After several hours, filter off the precipitate and drain it as completely as possible with the aid of suction. Wash the precipitate four times with 25-cc. portions of alcohol and twice with ether. Recrystallize the salt by dissolving each 10 gms. of solid in 15 cc. of water and precipitating with 35 cc. of alcohol. The dry salt keeps very well, but the aqueous solution decomposes gradually. To obtain the best results, the reagent should be prepared freshly by dissolving 1 gm. of the salt in 10 cc. of water.

Reactions in the Dry Way

Potassium compounds color the non-luminous flame violet. The presence of very small amounts of sodium obscures the violet color, but if the flame is viewed through cobalt glass or indigo solution, the reddish-violet potassium rays pass through, while the yellow sodium rays are completely absorbed.

Flame Spectrum. — Potassium gives a characteristic flame spectrum. A double red line, 769.9 $\mu\mu$ and 766.5 $\mu\mu$ (appearing as a single line with weaker dispersion), and a faint violet line, 404.4 $\mu\mu$, appear at comparatively low temperatures. With a hotter flame, other lines are visible in the yellow, 583.2 $\mu\mu$; 580.2 $\mu\mu$ and 578.2 $\mu\mu$, and in the green, 535.1 $\mu\mu$ and 511.3 $\mu\mu$ (see chart, Frontispiece).

Gooch and Hart * were able to detect 0.001 mg. of pure potassium as chloride in 0.02 cc. water, but the presence of one hundred times as much sodium caused the potassium lines to disappear unless the sodium rays were deflected from the field.

SODIUM, Na. At. Wt. 23.00

Sp. Gr. 0.97. M. Pt. 95.6° C.

Occurrence. — Sodium occurs very extensively in nature. Its most important mineral is halite, or rock salt (NaCl), isometric system. Halite is found in very large deposits, often quite pure, but usually contaminated with clay, anhydrite, and gypsum. Dissolved sodium chloride is present in large amounts in the ocean, and in many salt

* *Z. anal. Chem.*, **36** (1897), 390.

springs. Sodium also occurs in nature in the form of carbonate, as thermonatrite ($Na_2CO_3 \cdot H_2O$), orthorhombic; natron or soda ($Na_2CO_3 \cdot 10\ H_2O$), monoclinic; trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2\ H_2O$), monoclinic; as nitrate in Chili saltpetre, or soda nitre ($NaNO_3$), hexagonal, rhombohedral; as cryolite (Na_3AlF_6), triclinic; in many silicates as albite ($NaAlSi_3O_8$), triclinic; and as tinkal, borax ($Na_2B_4O_7 \cdot 10\ H_2O$), monoclinic.

Reactions in the Wet Way

1. **Potassium Pyroantimonate,*** $K_2H_2Sb_2O_7$, produces in neutral or weakly alkaline solutions of sodium salts a heavy, white, crystalline precipitate, which is formed more quickly by rubbing the inside walls of the vessel with a glass rod:

$$K_2H_2Sb_2O_7 + 2\,NaCl = \mathbf{Na_2H_2Sb_2O_7} + 2\,KCl.$$

The test must not be made in an acid solution, for in that case an amorphous precipitate of pyroantimonic acid will be formed:

$$K_2H_2Sb_2O_7 + 2\,HCl = \mathbf{H_4Sb_2O_7} + 2\,KCl.$$

Ammonium salts of strong acids also give an amorphous precipitate of pyroantimonic acid on standing; this is due to the hydrolysis of the ammonium salt whereby the solution becomes slightly acid. Furthermore, no other metals than the alkalies should be present, because they also cause precipitates — amorphous ones for the most part.

2. **Tartaric Acid** and **Chloroplatinic Acid** do not precipitate sodium salts, the sodium salts of these acids being soluble in alcohol as well as in water. (Note difference from potassium.) Sodium chloroplatinate is orange in color.

3. **Hydrochloric Acid** and **Alcohol** precipitate sodium chloride. Sodium chloride is prepared pure for chemical purposes by passing hydrogen chloride gas into the saturated aqueous solution of the salt and expelling the moisture and hydrochloric acid from the crystals by heating them. If dry hydrogen chloride is passed into an alcoholic solution of a sodium salt, less than 1 mg. of sodium will remain in solution.

Sodium Peroxide, Na_2O_2

This substance, which is now used commercially on account of its energetic oxidizing power, is obtained as a heavy, yellow powder, by burning dry sodium in the air. It shows the following characteristic reactions:

* For the preparation of this reagent see page 77 and under Antimony.

Behavior toward Water. — If a little water is added to some of this substance in a test-tube, considerable heat is evolved and oxygen gas is liberated (sufficient to ignite a glowing splinter*). Water decomposes the sodium peroxide, according to the equation

$$Na_2O_2 + 2\,H_2O = 4\,NaOH + H_2O_2.$$

But on account of the heat of the reaction a part of the hydrogen peroxide is decomposed into water and oxygen, $2\,H_2O_2 \rightarrow 2\,H_2O + O_2\uparrow$.

If the solution is kept cold, which can be done by throwing the sodium peroxide in small portions into ice-water, it will dissolve with scarcely any evolution of oxygen, to a clear, strongly alkaline liquid, which gives, as before, all the reactions of hydrogen peroxide.

If some sodium peroxide is placed on a watch-glass under a bell-jar and near an evaporating-dish containing water, the sodium peroxide in twelve hours will completely change over to a pure white hydrate ($Na_2O_2 \cdot 8\,H_2O$), which will dissolve in water without decomposition at the ordinary temperature. By standing in a desiccator over sulfuric acid, the octohydrate is changed to $Na_2O_2 \cdot 2\,H_2O$.

Reactions of Hydrogen Peroxide

(*a*) *In Acid Solution*

If the solution obtained by the action of water on sodium peroxide is used for these tests, it must be acidified with dilute sulfuric acid, care being taken to keep the solution cool.

1. **Titanium Sulfate** gives a distinct yellow color, caused by the formation of pertitanic acid,

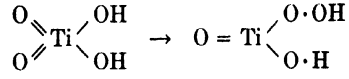
$$Ti^{++}_{++} + H_2O_2 + 2\,H_2O \rightarrow 4\,H^+ + H_2TiO_4.$$

This is the most delicate test for hydrogen peroxide. The titanium sulfate solution for this reaction may be prepared by fusing one part of commercial titanium dioxide with 15–20 parts of potassium pyrosulfate and dissolving the fusion, after cooling, in cold, dilute sulfuric acid. It may also be prepared by heating titanium dioxide with concentrated sulfuric acid, until a clear solution is obtained, cooling and diluting carefully with water.

The addition of caustic alkali, ammonia or ammonium carbonate gives a yellowish-orange precipitate which redissolves in an excess of the reagent. Classen has used this reaction as a method for separating

* This will sometimes cause an explosion. Commercial sodium peroxide often contains metallic sodium, which with water forms hydrogen; thus both hydrogen and oxygen are set free at the same time, and the glowing splinter may then cause an explosion. (Private communication from E. Constam.)

titanium from ferric iron.* Some chemists prefer to write the formula of pertitanic acid as $TiO_2 \cdot H_2O_2$, which assumes a true peroxide structure instead of hexivalent titanium. Possibly a condition of equilibrium exists between the two structures:



2. **Chromic Acid.** — If the acid solution of hydrogen peroxide is shaken with a little ether (free from alcohol) and a trace of potassium dichromate is added, after which the mixture is again shaken, the upper layer of ethereal solution will be colored a beautiful blue, owing to the formation of chromium peroxide (cf. p. 18).

This test is very sensitive and will detect as little as one-tenth milligram of H_2O_2. In carrying out this test, a *blank* test must always be tried with the ether alone, because after standing in the air, it is likely to contain some ethyl peroxide $(C_2H_5)_4O_3$, (?) which gives the test. It is possible to free the ether from this peroxide by letting it stand over night in contact with sodium and then redistilling it.

3. **Permanganic Acid** in acid solution will be decolorized, with evolution of oxygen:

$$2\,MnO_4^- + 5\,H_2O_2 + 6\,H^+ \rightarrow 2\,Mn^{++} + 8\,H_2O + 5\,O_2\uparrow.$$

Similar to the permanganate, many other oxides are reduced by hydrogen peroxide, with evolution of oxygen; e.g., Ag_2O, Pb_3O_4, PbO_2, MnO_2, Co_2O_3, etc.:

$$Ag_2O + H_2O_2 \rightarrow H_2O + O_2\uparrow + 2\,Ag$$
$$MnO_2 + H_2O_2 + 2\,H^+ \rightarrow Mn^{++} + 2\,H_2O + O_2\uparrow$$
$$Co_2O_3 + H_2O_2 + 4\,H^+ \rightarrow 2\,Co^{++} + 3\,H_2O + O_2\uparrow.$$

4. **Potassium Ferricyanide** and **Ferric Chloride.** — If a trace of potassium ferricyanide is added to a very dilute and nearly neutral solution of ferric chloride, so that the solution appears a distinct yellow, and a nearly neutral solution of hydrogen peroxide is then added, the mixture will soon assume a green tint, and finally, on standing, Prussian blue will separate out. The potassium ferricyanide is reduced by the hydrogen peroxide to potassium ferrocyanide, which forms Prussian blue with the ferric chloride.

$$2\,[Fe(CN)_6]^{---} + H_2O_2 \rightarrow 2\,[Fe(CN)_6]^{--} + O_2\uparrow + 2\,H^+$$

and

$$3\,[Fe(CN)_6]^{--} + 4\,Fe^{+++} \rightarrow Fe_4[Fe(CN)_6]_3.$$

* Ber., **21** (1888), 370.

According to Schönbein, as little as 0.02 mg. H_2O_2 per liter may be detected by this reaction. As many other substances ($SnCl_2$, SO_2, etc.) will reduce potassium ferricyanide to potassium ferrocyanide, this reaction alone is not always a reliable test.

5. **Starch Paste** and **Potassium Iodide.** — If to an acid solution containing starch paste and potassium iodide some hydrogen peroxide is added, a blue color will at once appear:

$$2\,KI + H_2O_2 = 2\,KOH + I_2.$$

By means of this reaction, 0.05 mg. per liter of hydrogen peroxide may be detected.

(b) In Alkaline Solution

1. **Gold Chloride** by means of hydrogen peroxide at ordinary temperatures will be reduced to metal, with evolution of oxygen. The gold usually separates in a very finely divided state, and appears brown by reflected light and greenish blue by transmitted light:

$$2\,Au^{+++} + 3\,H_2O_2 + 6\,OH^- \rightarrow 2\,Au + 6\,H_2O + 3\,O_2\uparrow.$$

If very dilute gold solutions are used, the metal sometimes separates out in the form of a yellowish film adhering to the sides of the test-tube.

2. **Salts of Manganese** and **Cobalt** give dark-colored precipitates:

$$Mn^{++} + 2\,OH^- + H_2O_2 \rightarrow H_2O + \underset{\text{Brown}}{MnO(OH)_2};$$

$$2\,Co^{++} + 4\,OH^- + H_2O_2 \rightarrow 2\,\underset{\text{Black}}{Co(OH)_3}.$$

Hypochlorites give the same reactions with manganese and cobalt salts, but they do not give the reaction with gold chloride.

Ozone, O_3

Ozone is always formed when oxygen is exposed to the silent electric discharge. It is often present in oxygen that has been prepared electrolytically and, according to Brunck, is present to some extent in the gas prepared by ignition of potassium chlorate. Ozone is a strong oxidizing agent and behaves in many respects like hydrogen peroxide, with which it is often confused. Ozone may be distinguished from hydrogen peroxide as follows:

1. Ozone does not give a yellow coloration with titanium sulfate solution.

2. Ozone does not cause precipitation of gold from its solutions.

3. Ozone sets free iodine immediately from dilute, neutral potassium iodide solution.

4. Ozone liberates bromine from an acid solution of sodium bromide.

5. Ozone causes bright metallic silver at once to assume a steel-blue tint.

The sensitiveness of this last reaction is remarkable if carried out according to the directions of Manchot and Kampeschulte. Heat a bright piece of silver foil to about 240° and then expose it to the action of ozone; steel-blue spots with violet edges at once appear. This reaction does not take place with pure silver in the cold. If, however, the silver is polished by rubbing with emery paper, the reaction will then take place in the cold. Traces of iron oxide are left upon the silver from the emery and catalyze the reaction. Other oxides, Ag_2O, CoO, NiO, Bi_2O_3, Pb_3O_4, V_2O_5, MnO_2, CuO, ThO_2, CeO_2, TiO_2, WO_3, U_3O_8, and to a less degree MoO_3, HgO, CaO and BaO, have a similar effect. Thus if the silver is etched with nitric acid and is then dried, it will react with ozone in the cold.

The principal reactions of sodium are the

Reactions in the Dry Way

Sodium salt vapors color the non-luminous gas-flame a monochromatic yellow, which can be readily distinguished from the yellow flame of the gas in the following way: If we illuminate an orange-colored body (such as a stick of sealing-wax or a crystal of potassium dichromate) with white light (all glowing solid bodies emit white light), the red and orange rays will be reflected: the body appears orange. If these bodies are illuminated with the monochromatic sodium light, they can now only reflect yellow light: the bodies appear yellow (a delicate test).

Flame Spectrum. — A yellow double line (589.6 $\mu\mu$ and 587.0), coinciding with the D-line of the sun's spectrum. This is an extremely delicate reaction; 1×10^{-7} mg. of sodium can be recognized in the spectrum.

AMMONIUM, NH_4. At. Wt. 18.04

Occurrence. — In small amounts as carbonate and nitrite in the air; as ammonium chloride in the fissures of active volcanoes. Ammonium derivatives are formed by the decay of many organic substances containing nitrogen: albumin, urea, etc.,

$$CO(NH_2)_2 + H_2O = CO_2\uparrow + 2\,NH_3\uparrow,$$

and in a similar way by the dry distillation of many nitrogenous substances, such as coal, horn, hair, etc.

Although ammonium itself is known only in the form of its amalgam, we are justified in considering it as a metal, in the first place because the

electrolysis of ammonium salts causes the setting free of the cation $NH_4^+(NH_3 + H^+)$ at the same time that the corresponding anion is set free; and, further, because the ammonium salts are isomorphous with potassium salts.

Reactions in the Wet Way

1. **Strong bases,** NaOH, KOH or $Ca(OH)_2$, added to an ammonium salt in the presence of a little water cause the evolution of ammonia on heating; the gas can be recognized by its odor, by fumes of ammonium chloride being formed when a rod moistened with 12 N hydrochloric acid is placed in contact with the vapors, by its turning red litmus blue; or by the blackening of mercurous nitrate paper:

$$2\,Hg_2(NO_3)_2 + 4\,NH_3 + H_2O = 3\,NH_4NO_3 + O\begin{matrix}\diagup\,Hg\,\diagdown\\ \diagdown\,Hg\,\diagup\end{matrix}NH_2 \cdot NO_3 + 2\,Hg.$$

Black

The reaction of strong bases upon ammonium salts may be explained on the basis of the laws of chemical equilibrium. Ammonia, NH_3, is a gas which is very soluble in cold water and insoluble in boiling water. One volume of water at 0° and 760 mm. dissolves 1300 volumes of the gas; at 20° it dissolves 710 volumes; at 100° all the gas can be expelled, there being no constant boiling mixture as in the case of hydrochloric acid (p. 60).

The solution of ammonia in water at the laboratory temperature is in equilibrium with ammonium hydroxide,

$$NH_4OH \rightleftarrows NH_3 + H_2O,$$

and, for this equilibrium, the mass-action expression (p. 14) is

$$\frac{[NH_3] \times [H_2O]}{[NH_4OH]} = k.$$

In a dilute solution of ammonia, the absolute quantity of water present is not changed much as a result of this equilibrium, so that when an accuracy corresponding to only two significant figures is desired, the H_2O member of this expression may be regarded as a constant (cf. p. 50) and the equilibrium expression then becomes

$$\frac{[NH]_3}{[NH_4OH]} = k_{NH_3} \quad (I).$$

The value of this constant has been found to be about 2.0 at 20°. The ammonium hydroxide, however, is not only in equilibrium with ammonia, but also with ammonium and hydroxyl ions,

$$NH_4OH \rightleftarrows NH_4^+ + OH^-,$$

and the mass-action expression of this equilibrium is

$$\frac{[NH_4^+]\,[OH^-]}{[NH_4OH]} = k_{base} \quad (II).$$

Moore * found the value of this constant to be about 5×10^{-5}. By adding $\frac{[NH_4OH]}{[NH_4OH]}$

* *J. Chem. Soc.*, **91** (1907), 1379.

to the left-hand member of equation (I) and its equivalent 1 to the right-hand member, we obtain the equation

$$\frac{[NH_3] + [NH_4OH]}{[NH_4OH]} = k_{NH_3} + 1 = k',$$

and

$$[NH_4OH] = \frac{[NH_3] + [NH_4OH]}{k'}.$$

Inserting this value for $[NH_4OH]$ in (II), we have

$$\frac{[NH_4^+]\,[OH^-]}{[NH_4OH] + [NH_3]} = k' k_{base} = K.$$

The value of this constant, K, at 18° is about 1.8×10^{-5}. If the concentrations of NH_4 salt and of the strong base are known, it is possible to compute how much NH_3 and NH_4OH will be liberated by means of this last constant, K.

The ammonium salts, unlike the free base, are largely ionized. When, therefore, an excess of OH^- is added to the solution of an ammonium salt, it is necessary, in order to establish equilibrium between NH_4^+ and OH^- for the greater part of the NH_4^+ to be converted into NH_4OH and then, to establish equilibrium between NH_4OH and NH_3, about two-thirds of the NH_4OH is changed into NH_3. By boiling the solution, the NH_3 is expelled and the above-mentioned states of equilibrium are disturbed and, as the final result, all of the original NH_4^+ becomes converted into NH_3 gas. Less than 0.2 mg. of ammonium can be detected by the litmus test when properly carried out. Care should be taken not to boil the solution so that some of the alkaline liquid becomes spattered into the nostril or upon the test paper.

Certain complex ammonia derivatives do not always evolve ammonia in this test. When pure mercuric amidochloride, $Hg\begin{matrix}NH_2\\Cl\end{matrix}$, is heated with caustic soda solution, a part of the nitrogen is evolved as ammonia, but if considerable mercuric salt is present the test is not obtained. This is because the mercuric amidochloride itself is only slightly soluble in water and, especially in the presence of an excess of mercuric compounds, furnishes scarcely any ammonium ions. If some potassium sulfide is added, however, the mercury is converted into more insoluble mercuric sulfide and the ammonia test is obtained:

$$\mathbf{Hg}\begin{matrix}\mathbf{NH_2}\\\mathbf{Cl}\end{matrix} + K_2S + H_2O = \mathbf{HgS} + KCl + KOH + NH_3\uparrow.$$

Water itself in some cases causes evolution of ammonia gas. It decomposes many nitrides, metal amides and cyanamides:

$$Mg_3N_2 + 6\,HOH = \mathbf{3\,Mg(OH)_2} + 2\,NH_3\uparrow,$$

$$NH_2Na + HOH = NaOH + NH_3\uparrow,$$

$$CaCN_2 + 3H_2O = \mathbf{CaCO_3} + 2\,NH_3\uparrow \text{ (at high temperatures).}$$

Calcium cyanamide

2. **Chloroplatinic Acid** gives a yellow crystalline precipitate:

$$H_2[PtCl_6] + 2\,NH_4^+ \rightarrow \mathbf{(NH_4)_2[PtCl_6]} + 2\,H^+.$$

This salt may be distinguished from the potassium salt —

(*a*) by its behavior on ignition; platinum alone is left behind:

$$3\,(NH_4)_2[PtCl_6] = 2\,N_2\uparrow + 2\,NH_3\uparrow + 18\,HCl\uparrow + 3\,Pt;$$

(*b*) by its behavior on treating with strong bases, whereby the smell of ammonia may be detected:

$$(NH_4)_2[PtCl_6] + 2\,NaOH = Na_2[PtCl_6] + 2\,H_2O + 2\,NH_3\uparrow.$$

3. **Tartaric Acid** produces, as with potassium, a white, crystalline precipitate of ammonium acid tartrate. The addition of a little sodium acetate, and rubbing the inside walls of the glass vessel with a stirring-rod, will hasten the formation of the precipitate:

$$H_2C_4H_4O_6 + NH_4^+ \rightarrow NH_4HC_4H_4O_6 + H^+.$$

The ammonium acid tartrate, like the corresponding potassium salt, is soluble in alkalies and mineral acids. It may be distinguished from the potassium salt by its behavior on ignition, carbon alone being left behind, and the residue not effervescing with hydrochloric acid; furthermore, ammonium acid tartrate will give off ammonia on being heated with caustic soda solution.

4. **Sodium Cobaltinitrite** gives a yellow precipitate similar to that produced with potassium. Before testing for potassium with this reagent, therefore, it is necessary to expel ammonium salts by evaporating the solution to dryness in a porcelain dish and heating until no more fumes are evolved. Small quantities of ammonium salts can be removed by boiling with a little sodium nitrite and acetic acid:

$$NH_4^+ + NO_2^- \rightarrow N_2\uparrow + 2\,H_2O.$$

The above-mentioned reactions are not suitable for the detection of the very small amounts of ammonia or of ammonium ions that are found in drinking-water. In such cases Nessler's reagent is used (an alkaline solution of potassium mercuric iodide). Large amounts of ammonia produce a brown precipitate,

$$2\,K_2HgI_4 + 4\,OH^- + NH_4^+ \rightarrow NHg_2I\cdot H_2O + 3\,H_2O + 4\,K^+ + 7\,I^-.$$

The precipitate is the iodide of the so-called *Millon's base;* its structural formula is probably $O\begin{matrix}\diagup Hg \diagdown \\ \diagdown Hg \diagup\end{matrix}NH_2\cdot I$. The corresponding black nitrate is formed in the test for ammonia with mercurous nitrate paper. The iodide of Millon's base has such a remarkable coloring power that mere traces of the ammonium ion can be detected by the yellow or brown color imparted to the solution. The test is obtained with ordinary distilled water. Since ammonia is often present in water as a result of its contact with decaying organic matter, the test for ammonia helps to determine whether a water is suitable for drinking. The test is called the *Nessler test,* and the alkaline solution of potassium mercuric iodide is called *Nessler's reagent.*

Water free from ammonia should be used in carrying out the Nessler test. Some sodium carbonate and a little potassium permanganate is added to ordinary distilled water, which is then redistilled, rejecting the first fourth and last sixth of the

distillate; the middle portion is the so-called *best water* of the chemical laboratory. For the most accurate work, Nessler's reagent should be prepared with such water (cf. p. 77) and the test should be made in a laboratory from which ammonium fumes are absent.

To test a water for the presence of traces of ammonium ions, the apparatus shown in Fig. 4 may be used. First of all, the apparatus itself must be freed from all traces of ammonium salt. To accomplish this, place about 50 cc. of water in the retort, add 1 cc. of a boiled, saturated solution of sodium carbonate and distill with the neck of the retort introduced well into the condenser tube. It is advisable not to use a rubber connection between the retort and the condenser; the condensed water serves to make a sufficiently tight connection.

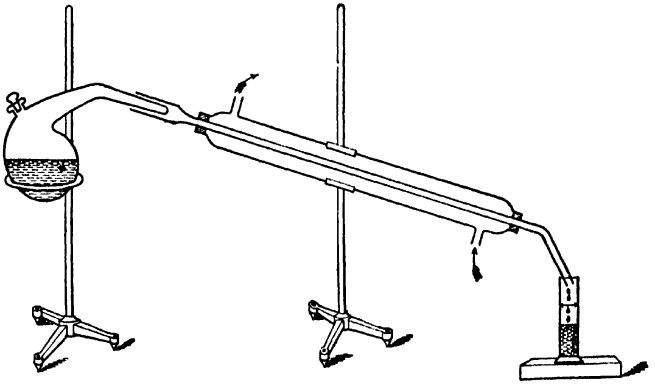


FIG. 4

Continue distilling until 50 cc. of the distillate placed in a white glass graduate or in a so-called Nessler tube, and treated with 1 cc. of Nessler reagent, will show no sign of color after standing five minutes. The apparatus is then ready for the test.

Empty the retort and refill it with 500 cc. of the water to be tested, add 1 cc. of the saturated sodium carbonate solution, distill and collect the first 50 cc. of distillate. If as much as 0.2 mg. of ammonium is present, a distinct precipitate forms on adding 1 cc. of Nessler's solution and stirring; a pronounced yellow color is obtained with much smaller quantities. If mere traces of ammonium are present, the yellow color appears only on standing. By comparing the depth of color with that similarly produced with known quantities of ammonium chloride, a very close estimate of the exact quantity of ammonium present can be made.

6. Picric acid, sodium tungstate and phosphomolybdic acid give precipitates as with potassium ions. Perchloric acid and potassium pyrantimonate do not give precipitates.

7. **Potassium iodide** and **sodium hypochlorite** solutions cause the precipitation of black nitrogen iodide:

$$2\,NH_4^+ + 2\,I^- + 2\,ClO^- \rightarrow \mathbf{NHI_2} + NH_3 + 2\,Cl^- + 2\,H_2O.$$

To make the test, which is a sensitive one, the neutral or alkaline solution of the ammonium salt is treated with a few drops of 10 per cent potassium iodide and a drop of saturated sodium hypochlorite solution.

8. **Paranitrodiazobenzene** solution in the presence of alkali gives a reddish yellow, flocculent precipitate, and the solution becomes yellow or red. The reaction depends upon the formation of an ammonium salt of *p*-nitrophenylnitrosamine.*

Reactions in the Dry Way

All ammonium salts are relatively unstable compounds, the degree of stability depending, in general, upon the strength of the acid which is combined with the ammonium. The carbonate decomposes appreciably at ordinary temperatures and when exposed to the air gradually disappears as ammonia, carbon dioxide and water. Heating in a closed tube causes the decomposition of all ammonium salts and either ammonia or some other volatile nitrogen compound escapes.

If the acid is volatile at the decomposition temperature, the whole salt is volatilized, often without first melting, and when the vapors of ammonia and acid are cooled the solid again forms. This explains the ammonium fumes that result when ammonium salts are expelled from a solid residue obtained by evaporation of a solution, and it explains the sublimate formed when ammonium chloride is heated in a closed tube. The acids which form salts that are not volatilized are boric, phosphoric, chromic, molybdic, tungstic and vanadic acids.

It must be remembered, however, that ammonia with its negative valence of three contains nitrogen in its lowest state of oxidation. When the decomposition of the original ammonium salt takes place, therefore, there is often an oxidation of the nitrogen. Thus the decomposition of the nitrate results in the formation of nitrous oxide, N_2O, and the decomposition of the nitrite, sulfate and dichromate yields nitrogen gas.

The closed tube reactions of typical ammonium compounds may be expressed by the following equations:

$$NH_4Cl \rightleftarrows NH_3 + HCl,$$

$$NH_4NO_3 = 2\,H_2O + N_2O,$$

$$NH_4NO_2 = 2\,H_2O + N_2,$$

$$3\,(NH_4)_2SO_4 = N_2 + 4\,NH_3 + 6\,H_2O + 3\,SO_2,$$

$$(NH_4)_2C_2O_4 = 2\,NH_3 + H_2O + CO + CO_2.$$

* Riegler, *Chem.-Ztg.*, 21, Rep. 307.

Toward the last some dicyanogen, $(CN)_2$, is formed from the oxalate.

$$NaNH_4HPO_4 \cdot 4\,H_2O = NH_3 + 5\,H_2O + NaPO_3,$$

$$2\,(NH_4)_3PO_4 = 6\,NH_3 + 2\,H_2O + 2\,HPO_3,$$

$$(NH_4)_2Cr_2O_7 = 4\,H_2O + N_2 + Cr_2O_3.$$

In this last reaction, the chromic oxide remains as a voluminous mass looking something like green tea. A realistic volcano effect can be obtained by making a mound of ammonium dichromate around a piece of paper and then setting fire to the latter.

Ammonium salts do not impart a characteristic color to the flame; the border of the flame is tinged slightly greenish.

MAGNESIUM, Mg. At. Wt. 24.32

Sp. Gr. = 1.75. M. Pt. = 632.6° C.

Occurrence. — Magnesium compounds are found very abundantly in nature. The most important minerals are magnesite, $MgCO_3$, rhombohedral, isomorphous with calcite; dolomite, $(Ca,Mg)CO_3$; brucite, $Mg(OH)_2$, rhombohedral; carnallite, $KMgCl_3 + 6\,H_2O$, orthorhombic; kieserite, $MgSO_4 + H_2O$, monoclinic; epsomite, $MgSO_4 + 7\,H_2O$, orthorhombic; spinel, $MgAl_2O_4$, isometric, isomorphous with magnetite, Fe_3O_4, and with chromite, $FeCr_2O_4$. Magnesium also occurs in a great many silicates. Thus almost all the minerals of the olivine group contain more or less magnesium. To this group belong forsterite, Mg_2SiO_4; monticellite, $CaMgSiO_4$; and olivine, $FeMgSiO_4$; all orthorhombic. An important decomposition product of the olivine minerals is serpentine, $Mg_3H_4Si_2O_9$. Almost all the minerals of the pyroxene-amphibole group, which are all related to orthorhombic enstatite, $MgSiO_3$, contain magnesium: augite, $MgAl_2SiO_6$; hornblende, an isomorphous mixture of $Mg_3CaSi_4O_{12}$ and 2 $(MgAl_2SiO_6)$; and tremolite, $CaMg_3Si_4O_{12}$, all three forming monoclinic crystals. Asbestos is a variety of tremolite with very fine fibers. Meerschaum is a magnesium silicate of the composition $H_4Mg_2Si_3O_{10}$, and is quite similar to talc, $H_2Mg_3Si_4O_{12}$, sometimes called steatite. Magnesium also occurs in the vegetable kingdom, being an essential constituent of the complex organic compound chlorophyll.

Properties of Magnesium. — Magnesium is a silver-white metal. It decomposes water very slowly, forming an oxide, MgO, which is only slightly soluble in water, forming magnesium hydroxide; the small quantity that dissolves is largely ionized, so that the solution has a faint alkaline reaction. Magnesium also burns in the air giving a dazzling white light and forming the oxide. Magnesium reacts directly with nitrogen at 300° C., forming magnesium nitride (Mg_3N_2), which is

readily decomposed by water, forming magnesium hydroxide and ammonia:

$$\mathbf{Mg_3N_2} + 6\,HOH = \mathbf{3\,Mg(OH)_2} + 2\,NH_3\uparrow.$$

The salts of magnesium are almost all colorless, soluble in water and have a bitter taste. The solubility products of magnesium hydroxide, carbonate, phosphate, arsenate and arsenite are so small that these substances may be regarded as insoluble. The sulfide, which can be prepared only in the dry way, is completely decomposed by water into hydroxide and hydrogen sulfide (hydrolysis). If an aqueous solution of magnesium chloride be evaporated to dryness on the water-bath, there is no hydrolytic decomposition, the residual salt, $MgCl_2 + 6\,H_2O$, dissolves in water, forming a perfectly clear solution. On heating the chloride containing the water of crystallization to 106° and higher, however, hydrochloric acid fumes escape and a basic magnesium chloride insoluble in water is left behind:

$$2\,MgCl_2 + H_2O \rightarrow \begin{matrix} Mg\diagup Cl \\ \quad\quad O \\ Mg\diagdown Cl \end{matrix} + 2\,HCl.$$

When a saturated solution of magnesium chloride is mixed with magnesium oxide, the mixture soon solidifies, forming a mass hard as stone, known as *magnesia cement*, consisting of basic magnesium chloride.

Reactions in the Wet Way

1. **Strong Bases,** such as the soluble hydroxides of sodium, potassium and barium, precipitate white, gelatinous magnesium hydroxide, and the precipitation is practically complete in the absence of ammonium salts or if the ammonium salt is all decomposed by boiling with an excess of the strong base (cf. pp. 19, 47).

$$Mg^{++} + 2OH^- \rightarrow \mathbf{Mg(OH)_2}.$$

The solubility product of magnesium hydroxide (cf. p. 22) is about 3.4×10^{-11} at the laboratory temperature. The saturated solution of magnesium hydroxide in pure water contains about 0.0002 mole or 0.012 gm. $Mg(OH)_2$ per liter. In the presence of an excess of OH^-, the solubility of the magnesium hydroxide is much less, as a result of the common ion effect (cf. p. 46), and it is possible, by keeping the volume of the solution small and using a slight excess of the reagent, to leave less than 1 mg. of magnesium in solution.

The precipitation of magnesium hydroxide by means of the slightly ionized ammonium hydroxide can never be made complete, and if the solution already contains ammonium ions in sufficient excess, no precipitation of magnesium hydroxide takes place. Moreover if a precipitate of magnesium hydroxide is boiled with a

solution of an ammonium salt, such as ammonium chloride, the precipitate dissolves. This behavior is due to the fact that the ionization of ammonium hydroxide (cf. p. 19 and p. 88) is repressed to such an extent, as a result of the common ion effect, that not enough OH^- ions are present at any one time to satisfy the solubility product of magnesium hydroxide, and even the OH^- from the $Mg(OH)_2$ must be in equilibrium with the NH_4^+ ions from NH_4Cl.

Formerly, the non-precipitation of magnesium by ammonium hydroxide was explained by the assumption that complex salts such as $NH_4[MgCl_3]$ or $(NH_4)_2[MgCl_4]$ were formed, but this explanation has proved untenable.*

2. **Mercuric Oxide** heated with solid magnesium chloride converts the latter into magnesium oxide which does not dissolve appreciably in water. The mercuric chloride formed and the excess of mercuric oxide are volatilized.

3. **Ammonium Carbonate** precipitates, in the absence of other ammonium salts, a basic salt (usually only on boiling or after long standing). The composition of the precipitated salt varies with the temperature and the concentration of the solution, the following salt being often obtained:

$$4\,Mg^{++} + 4\,(NH_4)_2CO_3 + H_2O \rightarrow \mathbf{Mg_4(CO_3)_3(OH)_2} + CO_2\uparrow + 8\,NH_4^+.$$

The addition of an excess of ammonium carbonate reagent (p. 75) and an equal volume of 95 per cent alcohol causes the complete precipitation of magnesium as $MgCO_3 \cdot (NH_4)_2CO_3 \cdot 4\,H_2O$ from a cold, concentrated solution of magnesium salt.

The magnesium ammonium carbonate is fairly soluble in water and the solubility increases rapidly with rise of temperature. Thus no precipitate is obtained upon the addition of ammonium carbonate to a hot dilute solution of magnesium salt containing ammonium chloride and no alcohol. (Note difference from barium, strontium and calcium.)

4. **Sodium Phosphate** is the characteristic reagent for magnesium. It produces in solutions containing ammonium chloride, and in the presence of ammonia, a white crystalline precipitate (orthorhombic, hemimorphous) of magnesium-ammonium phosphate,†

$$Mg^{++} + NH_4^+ + PO_4^{---} \rightarrow \mathbf{MgNH_4PO_4}.$$

From very dilute solutions the precipitate separates only after standing some time, owing to the tendency to form supersaturated solutions. Rubbing the sides of the beaker with a glass rod hastens the formation of the precipitate.

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* Cf. Loven, *Z. anorg. Chem.*, **11** (1896), 404; Treadwell, *ibid.*, **37** (1903), **326**, and Herz, *ibid.*, **38** (1903), 138.

† Magnesium ammonium phosphate crystallizes with six molecules of water.

The table on p. 22 gives the solubility product of magnesium ammonium phosphate as 2.5×10^{-13}; about 0.0086 g. of the salt dissolves in a liter of water at the laboratory temperature. The solubility in water is increased by its tendency to undergo hydrolysis.

$$MgNH_4PO_4 + HOH \rightleftarrows Mg^{++} + HPO_4^{--} + NH_4OH. \qquad (I)$$

The tendency to undergo hydrolysis increases rapidly with rise in temperature (cf. p. 52). A similar decomposition is caused by hydrogen ions alone,

$$MgNH_4PO_4 + H^+ \rightleftarrows Mg^{++} + HPO_4^{--} + NH_4^+, \qquad (II)$$

which lessen the tendency for HPO_4^{--} to ionize; the precipitate, therefore, dissolves readily in the presence of any acid which is ionized more than HPO_4^{--}, even acetic acid (cf. p. 10). The presence of ammonium hydroxide prevents the hydrolysis, in accordance with the mass-action law. For this reason an excess of ammonium solution is usually added. Ammonium chloride, by virtue of the common ion effect, lessens the quantity of Mg^{++} ions required to reach the solubility product and causes reaction (II) to take place in the direction right to left; but, on the other hand, it should favor reaction (I) somewhat, because it represses the ionization of ammonium hydroxide. As a matter of fact ammonium salts usually retard the formation of the precipitate, but do not eventually make it more soluble if an excess of ammonia is present.

Neubauer * has shown that the conditions are still more complicated on account of the tendency for gelatinous $Mg_3(PO_4)_2$ and crystalline $Mg(NH_4)_4(PO_4)_2$ to form. Tertiary magnesium phosphate, $Mg_3(PO_4)_2$, is formed in cold, strongly ammoniacal solutions containing but little ammonium salts. The monomagnesium-tetrammonium phosphate is formed in neutral or slightly alkaline solutions containing considerable ammonium salts. B. Schmitz † has shown that beautifully crystalline precipitates can be obtained in the presence of ammonium salts by adding sodium or ammonium phosphate to the boiling, acid solution of the magnesium salt. Then, on adding one-third the solution's volume of 6 N ammonia and allowing the solution to cool, complete precipitation, as $MgNH_4PO_4 \cdot 6\,H_2O$, takes place.

Reactions in the Dry Way

All magnesium salts are more or less changed on heating in the air, leaving behind the oxide or an insoluble basic salt. On charcoal with sodium carbonate before the blowpipe, magnesium compounds are changed to white magnesium oxide, which is strongly luminous when hot. Calcium, strontium, and aluminium compounds behave the same way. The magnesium salts are non-volatile, do not color the flame, and give no flame spectrum, but do give a characteristic spark spectrum.

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* *Z. angew. Chem.* (**1898**), 439. Cf. Gooch and Austin, *Z. anorg. Chem.*, **20**, 121.

† *Z. anal. Chem.* (**1906**), 512. Cf. Jorgensen, *ibid.* (**1906**), 278.

Detection and Separation of Magnesium and the Alkalies in the Presence of One Another

All of the typical reactions that have been described for magnesium can be used for separating magnesium from the alkalies. The test for ammonium is always carried out with some of the original substance or solution.

Ordinarily in qualitative analysis, it is customary either to test for magnesium in one portion of the solution by means of sodium phosphate and for sodium and potassium in another portion, or to precipitate the magnesium as carbonate and test for sodium and potassium in the filtrate. In this last method the magnesium can be precipitated with the alkaline earths. If this is done, the test for magnesium is not made in the analysis of this group.

In all the principal systematic methods given in this book for the examination of the basic constituents, a very brief tabular outline will be given first with reference by numbers to the detailed directions that immediately follow.

TABLE I. — ANALYSIS OF GROUP V

METHOD A

<table>
<tr>
<td rowspan="2">NH_4+. Test a portion of the original substance for NH_4+ by boiling with NaOH. (1)</td>
<td rowspan="2">Mg++. Test a part of the filtrate from Group IV, Method A, for Mg with NH_4OH and Na_2HPO_4. (2)</td>
<td colspan="2">Evaporate to dryness. Expel NH_4 salts. Dissolve in water, add $Ba(OH)_2$ and reject precipitate. Add HCl, NH_4OH and $(NH_4)_2CO_3$ and also reject this precipitate. Evaporate, expel NH_4 salts, dissolve in water, filter, and add $HClO_4$. Evaporate, add alcohol and filter. (3)</td>
</tr>
<tr>
<td>Precipitate: $KClO_4$. Dissolve in hot water and add $Na_3Co(NO_2)_6$. Yellow precipitate is $K_2NaCo(NO_2)_6$. (4)</td>
<td>Filtrate: Saturate with HCl gas. Filter off NaCl and reject filtrate. Dissolve in water and add $K_2H_2Sb_2O_7$. Crystalline precipitate is $Na_2H_2Sb_2O_7$. (5)</td>
</tr>
</table>

PROCEDURE

1. *Test for Ammonium.* Place a little of the original substance (corresponding to about 0.25 gm. of solid) in a test-tube, add about 2 cc. of 6 N sodium hydroxide, heat nearly to boiling and hold a piece of red litmus paper, wrapped around the end of a stirring rod, in the escaping vapors. Take care not to allow any of the caustic alkali to come in contact with the litmus either by spattering or by allowing the paper to touch the sides of the test-tube. A good idea of the quantity of ammonium present can be obtained from the odor. If it is desired to test for traces of ammonium, carry out the Nessler test as described on p. 95.

2. *Test for Magnesium.* Dissolve the substance in as little water as possible, or, if a solution, evaporate to dryness, moisten with 6 N hydrochloric acid, heat gently, dissolve in a little water and filter if necessary. The addition of the acid is not usually necessary, but sometimes, when calcium has previously been removed as oxalate, a difficultly soluble oxalate of magnesium and ammonium is formed which is best dissolved by treatment with acid before adding water. If the solution to be tested contains considerable ammonium salt, it is usually best to expel it by igniting the residue obtained by evaporation; the treatment of the residue with hydrochloric acid is then absolutely necessary, in order to decompose basic magnesium salts which are formed during the ignition.

If ammonium chloride is not already present, add half the solution's volume of normal ammonium chloride and enough ammonia to make the solution distinctly ammoniacal. If a precipitate of magnesium hydroxide is formed, add more ammonium chloride to dissolve it. A flocculent precipitate produced at this point may be aluminium hydroxide or silica. Such a precipitate should be filtered off and discarded. To the clear ammoniacal solution add a little sodium phosphate solution and rub, with a rounded stirring rod, the inside walls of the vessel containing the solution. If as much as a few tenths of a milligram of magnesium is present per 100 cc., a crystalline precipitate of magnesium ammonium phosphate should form within a few minutes. In case no precipitate is noticeable, set the beaker aside and allow it to stand overnight. Traces of magnesium phosphate will usually form on the sides of the beaker where it was scratched by the stirring rod.

If the precipitate does not appear distinctly crystalline, it may contain aluminium phosphate. In such cases filter off the precipitate and redissolve it in 6 N acetic acid, which will not dissolve aluminium phosphate but readily dissolves magnesium ammonium phosphate. Heat the solution nearly to boiling, add a liberal excess of ammonia and allow to cool; a crystalline precipitate should be obtained by this treatment.

3. *Test for Sodium and Potassium.* Before testing for sodium and potassium it is best to remove the magnesium. Evaporate the solution to dryness in a porcelain or platinum dish and gently ignite the residue to expel ammonium salts. Dissolve the residue in a little water and, without paying any attention to any residue of basic magnesium salt, add barium hydroxide solution until strongly alkaline. Heat to boiling and filter off the precipitate, which may contain magnesium hydroxide, barium sulfate, if any sulfate ions were present, and barium carbonate from the contact of the barium hydroxide solution with the air. These operations should never be carried out in glass dishes because of the danger of obtaining alkali from the glass. Make the filtrate from the magnesium precipitate barely acid with hydrochloric acid and remove all barium ions by the addition of ammonia and ammonium carbonate. Filter off the precipitated barium carbonate, evaporate the filtrate to dryness and expel the ammonium salts by careful ignition. Dissolve the residue in a little water and make sure that all the barium was removed by adding a little more ammonium carbonate. Filter if necessary and again evaporate to dryness. Expel the ammonium salt by ignition, cool and wash down the sides of the dish with about 5 cc. of water to dissolve any ammonium salt that may possibly be left there. Evaporate to dryness again and expel the last traces of ammonium salts by igniting at a dull red heat until no more fumes are evolved. Dissolve the residue in a little water and filter the resulting solution through a small filter. A black residue is often due to carbonization of pyridine bases, which are commonly present to a slight extent in ammonia solutions.

Evaporate the solution just to dryness, add 5 to 15 cc. of 2 N perchloric acid and evaporate carefully, by keeping the dish in constant motion over a free flame, until dense fumes of perchloric acid are evolved. Cool completely and add 20 cc. of alcohol.

The perchloric acid solution must not be heated or concentrated by evaporation after the alcohol has been added or a dangerous explosion is likely to result.

Stir the solution and press down gently with a stirring rod upon any crystals that may be present. If after stirring a few minutes a residue of potassium perchlorate remains, add 3 cc. more of the perchloric acid reagent. Filter through a dry filter-paper and wash the precipitate with alcohol.

4. If the previous manipulation has been faulty, the precipitate obtained with perchloric acid may consist of ammonium perchlorate, and it is advisable, therefore, to confirm the potassium test. Dissolve the precipitate on the filter with as little hot water as possible, using not over 10 cc. at the most. Add the water in small portions around the top of the filter-paper and pass the first filtrate through the filter a second time. Add 3 to 5 cc. of sodium nitrite reagent and 2 to 3 cc. of 6 N acetic acid and boil gently for about five minutes. The boiling with nitrous acid serves to decompose any ammonium salt present; it will cause the decomposition of as much as 30 mgs. of ammonium ions.

$$NH_4^+ + NO_2^- \rightarrow N_2 \uparrow + 2\,H_2O.$$

Cool the solution and add a little sodium cobaltic nitrite reagent. A yellow precipitate of $K_2NaCo(NO_2)_6$ will form within ten minutes if as much as 0.3 mg. of potassium is present.

5. *Test for Sodium.* Pour the alcoholic filtrate from the perchlorate precipitate into a small Erlenmeyer flask, place the flask in cold water and saturate with dry hydrogen chloride gas. This gas may be prepared by dropping concentrated sulfuric acid into a flask containing common salt and concentrated hydrochloric acid and passing the escaping gas through concentrated sulfuric acid. In the presence of alcohol the hydrogen chloride will precipitate as little as 1 mg. of sodium ions as sodium chloride. Filter off the precipitated sodium chloride and wash it with a little alcohol. Dissolve it in a very little water, evaporate the solution to dryness, dissolve in 1 cc. of water and add twice as much potassium pyroantimonate reagent. A crystalline precipitate of sodium pyroantimonate can be obtained with as little as 1 mg. of sodium ions if the solution is allowed to stand overnight. Traces of many other elements, such as the alkaline earths, magnesium and aluminium also give precipitates with this reagent, but such precipitates are flocculent.

The final precipitates of potassium and sodium should always be submitted to the flame test in all cases of doubtful precipitation.

TABLE II. — ANALYSIS OF GROUP V

METHOD B

<table>
<tr><td>NH_4+. Test the original substance as in Method A, p. 101.</td><td colspan="3">Filtrate from Group IV, Method A, may contain Mg++, K+, Na+, NH_4+. Concentrate to 10 cc., add 15 cc. $(NH_4)_2CO_3$ and 15 cc. C_2H_5OH. (1)</td></tr>
<tr><td></td><td>Precipitate: $MgCO_3 \cdot (NH_4)_2CO_3 \cdot 4H_2O$. Dissolve in 6-normal H_2SO_4 and add an equal volume of C_2H_5OH. Filter, add NH_4OH and Na_2HPO_4 to precipitate Mg NH_4PO_4. (2)</td><td colspan="2">Filtrate: K+, Na+, NH_4+. Remove sulfate by a $BaCl_2$, remove Ba++ with $(NH_4)_2CO_3$. Expel NH_4+ salts and add $HClO_4$. (3)</td></tr>
<tr><td></td><td></td><td>Precipitate: $KClO_4$. Examine as in Method A, p. 102. (3)</td><td>Filtrate, Na+. Test for Na as in Method A, p. 102. (3)</td></tr>
</table>

PROCEDURE *

1. Concentrate the solution to a volume of about 10 cc. and filter if necessary. If ammonium salts are deposited it is best to remove them first as in Method A. Add to the concentrated solution 15 cc. of ammonium carbonate reagent and 15 cc. of alcohol, stir well, and allow the mixture to stand half an hour or longer. Filter off the precipitate of $MgCO_3 \cdot (NH_4)_2CO_3 \cdot 4H_2O$.

2. To confirm the magnesium test, dissolve the precipitate, which may contain alkaline-earth carbonate, in a little 6 N sulfuric acid and add an equal volume of alcohol. Any barium, strontium or calcium will be converted into insoluble sulfate by this treatment. Filter the solution if necessary and test for magnesium with sodium phosphate solution in the usual way.

3. *Test for Sodium and Potassium.* Evaporate the filtrate from the ammonium carbonate treatment to dryness in a small porcelain dish and heat the residue until no more white fumes are evolved from the heated bottom and sides of the dish. Keep the temperature below redness to avoid volatilizing alkali chloride and heat the sides as well as the bottom of the dish, which should be moved about over a small free flame. Cool, add 5 cc. of water, rinse with a very little water into a small flask and treat the boiling hot solution with barium chloride solution, drop by drop, until all sulfate is precipitated. Filter and precipitate the excess of barium with ammonium carbonate solution. After five minutes, heat to boiling and filter off the barium carbonate. Evaporate and expel ammonium salts as before. Cool, add 5 cc. of water and filter through a small filter. Evaporate again in a porcelain dish and ignite as before to make sure that the last traces of ammonium salt are removed.

To the ignited chloride residue, add 2–5 cc. of 6-normal perchloric acid and evaporate, by keeping the dish in motion over a free flame, until thick fumes of perchloric acid are evolved. Cool, and when at room temperature add 10–20 cc.

* Cf. SCHAFFGOTT, *Ann. Phys.*, **194** (1858), 482; GOOCH and EDDY, *Z. anorg. Chem.* (**1908**), 427; A. A. NOYES, *A Course of Instruction in the Qualitative Chemical Analysis of Inorganic Substances* (1920).

of 95 per cent ethyl alcohol. Stir for several minutes, filter and wash the precipitate with alcohol. Save the filtrate for the sodium test. Dissolve the potassium perchlorate precipitate in a few cc. of hot water, cool and add 5 cc. of sodium cobaltinitrite reagent. A yellow precipitate shows the presence of potassium.

Pour the alcoholic filtrate from the potassium perchlorate precipitate into a small flask and saturate it with dry HCl gas. Filter off the precipitated sodium chloride, wash it with a little alcohol and reject the filtrate. (A dangerous explosion will result if this filtrate is heated or evaporated.) Dissolve the sodium chloride in 10 cc. of water and evaporate the solution just to dryness. Add 1 cc. of water and a few drops of potassium hydroxide solution to make the solution alkaline. Add 2 cc. of potassium pyroantimonate solution and allow the mixture to stand for some time. A white crystalline precipitate shows the presence of sodium. If a flocculent precipitate is formed, the heavier sodium precipitate can usually be discovered if the mixture is shaken and after a few seconds decanted off from the heavier sodium pyroantimonate which usually adheres to the glass.

TABLE III ANALYSIS OF GROUP V

METHOD C

NH_4^+. Test the original substance as in Method A, p. 101.	Filtrate from Group IV, Method A, may contain Mg^{++}. K^+, Na^+, NH_4^+. Concentrate to 10 cc., add 15 cc. $(NH_4)_2CO$, and 15 cc. C_2H_5OH as in Method B. (1)	
	Precipitate: $MgCO_3(NH_4)_2CO_3.4\,H_2O$. Test as in Method B. (2)	Filtrate: K^+, Na^+, NH_4^+. Remove ammonium salts, add HCl and again ignite. Add 3 cc. of water and test one-third for potassium with $Na_3Co(NO_2)_6$ and the remaining solution for sodium with $K_2H_2Sb_2O_7$. (3)

(1) Proceed exactly as in Method B.

(2) Proceed exactly as in Method B.

(3) *Test for Sodium and Potassium.* Evaporate the filtrate to remove ammonium salts and ignite as described in Method B. Cool and add 5 cc. of 12-normal hydrochloric acid. (If a considerable residue of undissolved alkali chloride remains, heat the mixture to about 75° and stir with a glass rod. This serves to dissolve enough alkali chloride for the subsequent tests but if much sodium or potassium chloride is present at this stage the greater part is left undissolved so that it will not interfere. Decant the solution into another porcelain dish and wash the residue with 2 cc. more of the strong acid.) Evaporate the solution to dryness and ignite in the same way as before. Cool, add 3 cc. of water and pour the solution through a very small filter.

Take one-third of the solution and add an equal volume of sodium cobaltinitrite reagent. Allow to stand 10 minutes if no precipitate forms at once. Filter and wash thoroughly with water. Reject the filtrate. Treat the precipitate with 5 cc. of hot, 6-normal hydrochloric acid and evaporate the solution to a small volume. Moisten a platinum wire with hydrochloric acid and heat in the non-luminous flame until no coloration is produced. Then moisten the wire with the solu-

tion to be tested, heat in the flame and view through a thick piece of blue glass. Violet flame* through blue glass shows potassium.

To the remainder of the solution containing sodium and potassium, add potassium pyroantimonate solution and examine to see if a crystalline precipitate of sodium pyroantimonate is produced, as in Method B.

This last method is recommended by A. A. Noyes when a simple and rapid method of testing for sodium and potassium is desired.

The separation of the potassium and sodium can be accomplished by treatment with chloroplatinic acid instead of perchloric acid, but such a method is not suitable in ordinary qualitative analysis on account of the expense involved. The treatment is practically the same except that instead of evaporating till fumes of perchloric acid are evolved, the solution is evaporated just to dryness on the water-bath.

* The test should be tried with some pure potassium salt if the observer is not familiar with the flame test. The potassium salt is easily volatilized and the flame is not persistent.

GROUP IV. ALKALINE EARTHS

CALCIUM, STRONTIUM, BARIUM

GENERAL CHARACTERISTIC REACTIONS

The metals of the alkaline-earth group are bivalent and heavier than water, which they decompose slowly at ordinary temperatures, with evolution of hydrogen and formation of difficultly soluble hydroxides of strongly alkaline reaction (cf. p. 41). The salts are mostly colorless and very slightly soluble in water. The halogen compounds, nitrates, nitrites, and acetates are soluble in water. The carbonates are insoluble in water and are decomposed on ignition into carbon dioxide, and white, infusible, strongly luminous metallic oxide:

$$CaCO_3 \rightleftarrows CaO + CO_2 \uparrow .$$

Strontium carbonate is less readily decomposed than calcium carbonate, and barium carbonate loses its carbon dioxide only when heated to a white heat; its oxide is not very luminous.

The sulfates and oxalates are very difficultly soluble. The sulfate of barium is the most insoluble sulfate and calcium sulfate the most soluble; of the oxalates, the calcium salt is the most insoluble (cf. p. 21). The solubility of the strontium salt is always midway between that of the corresponding calcium and barium salt, for the atomic weight of strontium, of which the solubility is a function, lies midway between the atomic weights of barium and calcium. The halogen salts are volatile and impart a characteristic color to the flame.

The metals of this group form oxides of the general type RO, and peroxides corresponding to the formula RO_2. The latter, on treatment with acids, give hydrogen peroxide and salts corresponding to the oxide RO:

$$RO_2 + 2\,HCl = H_2O_2 + RCl_2.$$

Magnesium is more closely related to this group than to the alkali metals. It can be precipitated with this group if the group precipitant, ammonium carbonate, is added to the concentrated solution together with an equal volume of alcohol.

CALCIUM, Ca. At. Wt. 40.07

Sp. Gr. 1.58. M. Pt. 810° C.

Occurrence. — Calcium is widely distributed in nature. It is found in enormous deposits in all stratified formations as carbonate (limestone, marble, chalk), often rich in petrification. The carbonate,

$CaCO_3$, is dimorphous, crystallizing in rhombohedrons as calcite and in the orthorhombic system as aragonite. Calcium also occurs in large masses as sulfate, partly as monoclinic crystallizing gypsum, $CaSO_4 \cdot 2\,H_2O$, and partly as anhydrite, $CaSO_4$, which crystallizes in the orthorhombic system. Calcium also occurs as fluorite, CaF_2, which crystallizes in the isometric system, with perfect octahedral cleavage; as apatite, $3\,Ca_3(PO_4)_2 \cdot Ca\begin{matrix}\nearrow Cl \\ \searrow F\end{matrix}$, which belongs to the hexagonal system; and, finally, in innumerable silicates, such as the monoclinic wollastonite, $CaSiO_3$, and the triclinic anorthite, $CaAl_2Si_2O_8$. The calcium minerals are the principal representatives of several important isomorphous groups:

Calcite Group, Rhombohedral.		*Aragonite Group, Orthorhombic.*	
Calcite,	$CaCO_3$	Aragonite,	$CaCO_3$
Magnesite,	$MgCO_3$	Strontianite,	$SrCO_3$
Dolomite,	$\begin{matrix}Ca \\ Mg\end{matrix}\Big\} CO_3$	Witherite,	$BaCO_3$
		Cerussite,	$PbCO_3$
Siderite,	$FeCO_3$		
Smithsonite,	$ZnCO_3$		
Rhodochrosite.	$MnCO_3$		

Anhydrite Group, Orthorhombic.		*Apatite Group, Hexagonal.*	
Anhydrite,	$CaSO_4$	Apatite,	$3\,Ca_3(PO_4)_2 + Ca(ClF)$
Celestite,	$SrSO_4$	Pyromorphite,	$3\,Pb_3(PO_4)_2 + PbCl_2$
Barite,	$BaSO_4$	Mimetite,	$3\,Pb_3(AsO_4)_2 + PbCl_2$
Anglesite,	$PbSO_4$	Vanadinite,	$3\,Pb_3(VO_4)_2 + PbCl_2$

Metallic calcium is silver-white when pure. It oxidizes in the air forming calcium hydroxide, $Ca(OH)_2$, and calcium carbonate, $CaCO_3$. It decomposes water with evolution of hydrogen and formation of the hydroxide.

Calcium oxide, CaO, or *quicklime*, reacts readily with water liberating much heat (slaking of lime). The hydroxide (slaked lime) is much less soluble in water than are barium and strontium hydroxides and is formed upon the addition of alkali hydroxide to a concentrated solution of a calcium salt. Air-slaked lime contains calcium carbonate.

The chloride and the nitrate of calcium are soluble in absolute alcohol or in a mixture of equal parts alcohol and ether. Of the corresponding barium and strontium salts only the chloride of strontium is soluble in alcohol.

Calcium nitrate is much more soluble than barium nitrate in strong nitric acid and the chloride is much more soluble than barium chloride in hydrochloric acid.

Reactions in the Wet Way

1. **Ammonia,** in case it is free from carbonate, produces no precipitate with calcium salts; on standing in the air, however, carbonic acid is absorbed and a turbidity of calcium carbonate results.

2. **Ammonium Carbonate,** or any other soluble, normal carbonate, precipitates white calcium carbonate; the precipitate is voluminous and flocculent when it first forms, but soon becomes crystalline, particularly when in contact with boiling water.

$$Ca^{++} + CO_3^{--} \rightarrow \mathbf{CaCO_3}. \quad (I)$$

The precipitate is noticeably soluble in an aqueous solution of the ammonium salt of any strong acid:

$$\mathbf{CaCO_3} + 2\,NH_4^+ \rightarrow Ca^{++} + 2\,NH_3\uparrow + H_2O + CO_2\uparrow. \quad (II)$$

When ammonium carbonate is the precipitant, equation (II) is essentially the opposite to equation (I) and the mass-action law shows how the reaction can be made to go in either direction. An excess of ammonium carbonate will favor the progress of equation (I) and boiling with a large quantity of an ammonium salt such as ammonium chloride will cause equation (II) to go to completion.

Ammonium carbonate is an unstable substance (cf. p. 53). Commercial ammonium carbonate, often called ammonium sesquicarbonate, is a mixture of approximately equivalent quantities of ammonium bicarbonate, NH_4HCO_3, and ammonium carbamate, $NH_4CO_2NH_2$; the latter salt corresponds to normal ammonium carbonate less one molecule of water. Calcium carbamate is quite soluble in water but by contact with water at 60° it becomes changed to insoluble calcium carbonate. The ammonium carbonate reagent is prepared with 6 N ammonia instead of water; this prevents the hydrolysis of the salt and changes the bicarbonate to ammonium carbonate.

Calcium bicarbonate is soluble in water, so that any acid which is dissociated to a greater extent than HCO_3^- will exert a solvent effect upon calcium carbonate.

$$\mathbf{CaCO_3} + H^+ \rightleftarrows Ca^{++} + HCO_3^-.$$

Thus acetic acid dissolves calcium carbonate readily. Boiling the solution favors the progress of the reaction, as the HCO_3^- is also in equilibrium with H^+ and H_2CO_3 and the latter with H_2O and CO_2:

$$HCO_3^- + H^+ \rightarrow H_2CO_3 \rightarrow H_2O + CO_2\uparrow,$$

and the carbon dioxide can be expelled completely at 100° (cf. p. 15).

The precipitation of calcium carbonate from boiling, dilute solutions containing ammonium salts is always more or less incomplete, for the reasons that have just been given, but from cold, concentrated solutions containing considerable alcohol the precipitation is practically complete.

3. **Ammonium Oxalate** produces in neutral or alkaline solutions a precipitate of calcium oxalate, which when formed from cold solutions is composed of extremely fine crystals, hard to filter, while from hot solutions larger crystals are formed:

$$C_2O_4^{--} + Ca^{++} \rightleftarrows \mathbf{CaC_2O_4}.$$

Calcium oxalate is practically insoluble in water and acetic acid, but dissolves readily in mineral acids:

$$\mathbf{CaC_2O_4} + 2\,H^+ \rightleftarrows Ca^{++} + H_2C_2O_4.$$

Calcium oxalate, unlike calcium carbonate, does not dissolve in acetic acid for the following reasons: (1) The solubility product of calcium oxalate is about 3.8×10^{-9} while that of calcium carbonate is about 1.7×10^{-8} (p. 21) which shows that the oxalate is somewhat less soluble in water than the carbonate. (2) The ionization constant of HCO_3^- is 0.0_63 while that of $HC_2O_4^-$ is 0.0_45 and that of acetic acid is 0.0_418; this reason is sufficient to explain why acetic acid has little solvent effect upon calcium oxalate. To dissolve calcium oxalate readily it is necessary to use an acid strong enough to repress the ionization of the first hydrogen of oxalic acid, for which the ionization constant is 0.038. (3) The progress of the reaction cannot be aided, as in the case of the carbonate, by the loss of a volatile constituent.

Ammonia precipitates from such a solution calcium oxalate again, the excess of hydrogen ions, as well as the oxalic acid which was formed, being neutralized.

Calcium oxalate on being boiled with sodium carbonate solution is easily changed to carbonate:

$$\mathbf{CaC_2O_4} + CO_3^{--} \rightleftarrows \mathbf{CaCO_3} + C_2O_4^{--}.$$

This reaction takes place in the direction left to right when an excess of CO_3^{--} ions is present in spite of the fact that calcium oxalate is somewhat less soluble than calcium carbonate. This is in accordance with the mass-action law (p. 13). An excess of $C_2O_4^{--}$ ions will make the reaction take place in the direction right to left.

4. **Sulfuric Acid** produces a precipitate only in concentrated solutions:

$$CaCl_2 + H_2SO_4 \rightleftarrows 2\,HCl + \mathbf{CaSO_4}.$$

One hundred cc. water dissolves 0.214 gm. $CaSO_4 \cdot 2\,H_2O$ at 40°, but much less than 1 mg. will dissolve in the same quantity of alcohol. In the presence of a slight excess of sulfate ions, calcium sulfate is less soluble, but the behavior of calcium sulfate toward hydrogen ions is similar to that of calcium carbonate. Calcium acid sulfate is much more soluble than normal calcium sulfate, and any acid which is capable of repressing the ionization of HSO_4^- will exert a solvent effect upon $CaSO_4$. Sulfuric acid itself, or any other strong acid, can exert this solvent effect.

Calcium sulfate is also soluble in concentrated ammonium sulfate, owing to the formation of a complex anion:

$$CaSO_4 + (NH_4)_2SO_4 \rightarrow (NH_4)_2[Ca(SO_4)_2].$$

5. **Calcium Sulfate** solution produces no precipitation with calcium salts. (Note difference from strontium and barium.)

6. **Sodium Phosphate** (Na_2HPO_4) produces in neutral solutions a white, flocculent precipitate of secondary calcium phosphate:

$$Ca^{++} + HPO_4^{--} \rightarrow \mathbf{CaHPO_4}.$$

If ammonia is added to the solution at the same time, tertiary calcium phosphate will be precipitated:

$$HPO_4^{--} + OH^- \rightarrow H_2O + PO_4^{---}$$
$$3\,Ca^{++} + 2\,PO_4^{---} \rightarrow \mathbf{Ca_3(PO_4)_2}.$$

Both of these phosphates of calcium are dissolved by hydrogen ions. A glance at the table on p. 10 shows that even acetic acid will repress the ionization of $H_2PO_4^-$ to an extent such that it will exert a slight solvent action upon $CaHPO_4$ and upon $Ca_3(PO_4)_2$. Acetic acid in the presence of a soluble acetate, however, will not dissolve $Ca_3(PO_4)_2$ appreciably. From a solution obtained by dissolving calcium phosphate in acid, ammonia always precipitates the tertiary salt.

7. **Chromates of the Alkalies** do not precipitate calcium salts from dilute solution. (Note difference from barium and strontium.) In a *concentrated* solution of calcium salt to which potassium chromate has been added, a precipitate of calcium chromate, $CaCrO_4 \cdot 2\,H_2O$, forms slowly after some time, or immediately upon adding two or three volumes of alcohol. Adding ammonium hydroxide favors the precipitation but acetic acid prevents it.

8. **Absolute Alcohol,** or a mixture of equal parts of absolute alcohol and ether, dissolves both the nitrate and chloride of calcium.

All deliquescent salts, with the exception of potassium carbonate, dissolve in absolute alcohol. All other salts are, in general, insoluble, or very difficultly soluble, in absolute alcohol. An exception to this rule

is found in the case of mercuric chloride, which is not deliquescent, and is much more readily soluble in alcohol than it is in water.

9. **Potassium Ferrocyanide** gives with calcium salts a white crystalline precipitate of calcium-potassium ferrocyanide, $CaK_2[Fe(CN)_6] \cdot 3\,H_2O$. In the presence of ammonium salts, calcium-potassium-ammonium ferrocyanides are formed.

10. **Barium Fluoride** precipitates calcium fluoride, CaF_2. The presence of 0.8 mg. in 10 cc. of solution can be shown by this reagent.

11. **Water** decomposes the carbide, phosphide, and nitride of calcium at the ordinary temperature, as follows:

(*a*) The carbide:

$$CaC_2 + 2\,HOH = \mathbf{Ca(OH)_2} + \underset{\text{Acetylene}}{C_2H_2}\uparrow.$$

Acetylene is evolved by the reaction, a gas with a peculiar smell.* If this gas is conducted into an ammoniacal copper solution, it rapidly produces a red precipitate of copper acetylide. The latter compound is harmless while it is moist; but in the dry state it can be readily exploded by a blow, by rubbing, or by simply warming.

(*b*) The phosphide:

$$Ca_3P_2 + 6\,HOH = \mathbf{3\,Ca(OH)_2} + 2\,PH_3\uparrow.$$

The garlic-smelling phosphine gas which is evolved is spontaneously combustible, because it always contains a small amount of the spontaneously-combustible, liquid hydrogen phosphide (P_2H_4).

(*c*) The nitride:

$$Ca_3N_2 + 6\,HOH = \mathbf{3\,Ca(OH)_2} + 2\,NH_3\uparrow.$$

Reactions in the Dry Way

Calcium compounds, on being heated with sodium carbonate before the blowpipe, are changed to the white infusible oxide, which glows brightly when hot.

The volatile calcium compounds color the non-luminous gas flame brick-red.

Flame Spectrum. — Orange-yellow double line (620.3 $\mu\mu$, 618.2 $\mu\mu$) and a yellowish-green one (554.4 $\mu\mu$, 551.8 $\mu\mu$); both of these lines belong to calcium oxide. If calcium chloride wet with hydrochloric acid is placed in the flame, a number of other lines are seen; in the orange-yellow 646.6 $\mu\mu$, 606.9 $\mu\mu$, 604.5 $\mu\mu$ and 593.4 $\mu\mu$, in the yellow 581.7 $\mu\mu$ and 572.0 $\mu\mu$, in the violet, usually very difficult to see, 422.7 $\mu\mu$ (see spectroscopic chart, Frontispiece).

* Pure acetylene is odorless. Almost all calcium carbide contains a little calcium phosphide, which evolves phosphine on treatment with water.

STRONTIUM, Sr. At. Wt. 87.63

Sp. Gr. 2.5. M. Pt. 800° C.

Occurrence. — Strontium occurs quite commonly with calcium, but usually in much smaller amounts. There are only a few true strontium minerals. The most important of these are: Strontianite, $SrCO_3$, orthorhombic, isomorphous with aragonite; and celestite, $SrSO_4$, orthorhombic, isomorphous with barite.

Metallic strontium is described generally as a silver-white metal but some authorities ascribe to it the color of brass; the yellow tint is probably due to impurities. It is similar to calcium in its chemical behavior. The hydroxide is more soluble in water than calcium hydroxide is and it requires stronger heating to convert it into the oxide.

Reactions in the Wet Way

1. **Ammonia:** same as with calcium.
2. **Ammonium Carbonate:** same as with calcium.
3. **Ammonium Oxalate:** same as with calcium; but the strontium oxalate is somewhat soluble in acetic acid.
4. **Dilute Sulfuric Acid** produces a white precipitate of strontium sulfate:

$$SrCl_2 + H_2SO_4 = 2\,HCl + \mathbf{SrSO_4}.$$

Strontium sulfate is much less soluble in water than calcium sulfate (6900 parts of water at ordinary temperatures dissolve 1 part $SrSO_4$), but much more soluble than barium sulfate. It is somewhat soluble in boiling hydrochloric acid, and insoluble in ammonium sulfate. By boiling with a solution of ammonium or alkali carbonate solution, the strontium sulfate is changed to carbonate:

$$\mathbf{SrSO_4} + CO_3^{--} \rightleftarrows \mathbf{SrCO_3} + SO_4^{--}.$$

5. **Calcium Sulfate** solution produces in neutral or weakly acid solutions, *after some time,* a precipitate of strontium sulfate:

$$Sr^{++} + CaSO_4 = \mathbf{SrSO_4} + Ca^{++}.$$

6. **Chromates of the Alkalies** produce in dilute solutions no precipitate (thus differing from barium); but from concentrated solutions strontium chromate is precipitated. It is much less soluble in alcohol; 100 cc. of alcohol, 53 per cent by volume, will dissolve 0.002 gm. $SrCrO_4$ and 0.088 gm. of $CaCrO_4$ at room temperature; 100 cc. of 29 per cent alcohol will dissolve 0.132 gm. $SrCrO_4$ and 1.22 gms. $CaCrO_4$. The precipitate is quite soluble in acetic acid.

7. **Absolute Alcohol.** The nitrate is not deliquescent, and does not dissolve in absolute alcohol. Strontium chloride is slightly deliquescent; the anhydrous salt dissolves scarcely at all in absolute alcohol; but, on the other hand, 1 gm. of $SrCl_2 + 6\ H_2O$ dissolves in 116.4 gms. of cold alcohol and 262 gms. of boiling absolute alcohol. 100 cc. of 66 per cent alcohol dissolve about 50 gms. of $SrCl_2 \cdot 6\ H_2O$.

8. **Sodium Sulfite** precipitates strontium sulfite from neutral or acetic acid solutions; the precipitate is soluble in hydrochloric acid. The reagent used in making this test should be a concentrated, freshly-prepared, aqueous solution free from sulfate.

9. **Potassium Ferrocyanide** produces no precipitation.

Reactions in the Dry Way

Heated on charcoal before the blowpipe the strontium compounds behave similarly to the calcium compounds.

The volatile strontium salts color the non-luminous gas flame carmine red.

Flame Spectrum. — A number of lines in the red and orange yellow and one in the blue. No bands in the green. Red 686.3 $\mu\mu$, 674.7 $\mu\mu$, 662.8 $\mu\mu$, 649.9 $\mu\mu$; orange-yellow 646.5 $\mu\mu$, 635.1 $\mu\mu$, **606.0** $\mu\mu$; blue **460.7** $\mu\mu$.

BARIUM, Ba. At. Wt. 137.37

Sp. Gr. about 4.0. M. Pt. 850° (?) C.

Occurrence. — Like strontium, barium is almost always found associated with calcium, but only in small amounts. The most important barium minerals are: Witherite, $BaCO_3$, orthorhombic, ismorphous with aragonite; barite, or heavy spar, $BaSO_4$, orthorhombic, isomorphous with anhydrite; and the hydrous barium aluminium silicate, harmotome, $BaAl_2H_2Si_5O_{15} + 4\ H_2O$. Harmotome crystallizes in the monoclinic system, and belongs to the class of zeolites.

Metallic barium is usually described as of silver-white color but according to some observers it is gold-yellow. The hydroxide is more soluble in water than any other alkaline earth hydroxide and it melts at a red heat without being decomposed. Concentrated solutions of barium salts give precipitates of barium chloride upon the addition of strong hydrochloric acid and of barium nitrate upon the addition of strong nitric acid. Insoluble barium salts, therefore, dissolve more readily in dilute hydrochloric or nitric acid than in stronger acid.

Reactions in the Wet Way

1. **Ammonia** and **Ammonium Carbonate:** same as with calcium and strontium.

2. **Ammonium Oxalate:** same as with calcium and strontium, except that the barium oxalate formed is more soluble in water (1 gm. dissolves in 2.6 liters of cold water), and is readily dissolved by hot dilute acetic acid.

3. **Phosphates of the Alkalies:** same as with calcium.

4. **Chromates of the Alkalies** produce in neutral solutions of barium salts a yellow precipitate of barium chromate (thus differing from calcium and strontium),

$$Ba^{++} + CrO_4^{--} \rightleftarrows \mathbf{BaCrO_4}.$$

The table on p. 10 shows that $HCrO_4^-$ is ionized only to between 0.1 and 0.2 per cent in 0.1 N solution. In the presence of a stronger acid, its ionization becomes much less, and the equilibria

$$H^+ + CrO_4^{--} \rightleftarrows HCrO_4^- \text{ and } 2\,HCrO_4^- \rightarrow H_2O + Cr_2O_7^{--}$$

progress farther in the direction left to right than in pure water. The final equilibrium, however, also depends upon the concentration of CrO_4^{--} in the solution. In the case of strontium chromate, enough CrO_4^{--} ions are present in the saturated aqueous solution so that the formation of the $HCrO_4^-$ takes place to a considerable extent when a little acetic acid is added to the solution, and it is easy in this way to prevent the precipitation of as much as 0.5 gm. of strontium ions; barium chromate, on the other hand, is so much more insoluble that it takes considerable acetic acid to have an appreciable effect upon its solubility. Thus a small quantity of barium can be separated from quite a large quantity of strontium by adding CrO_4^{--} and a suitable quantity of acetic acid.

If a more highly ionized acid is present, such as hydrochloric acid, the barium will not be precipitated as chromate, but by adding sodium acetate (cf. p. 47) the concentration of the hydrogen ions can be reduced sufficiently to precipitate even a small quantity of barium as chromate.

5. **Dilute Sulfuric Acid** produces, in even the most dilute solutions, a precipitate of barium sulfate:

$$Ba^{++} + SO_4^{--} \rightarrow \mathbf{BaSO_4}.$$

According to the table on p. 21, 1 liter of pure water dissolves about 2.5 mgs. of barium sulfate. In a slight excess of sulfuric acid it is much less soluble by virtue of the common ion effect (p. 46). As with strontium and barium sulfates, the presence of an excess of hydrogen ions has a solvent action due to the formation of acid sulfate. This effect is appreciable with acids such as hydrochloric or nitric acid, but the solubility of barium sulfate is so slight that it requires treatment with hot, concentrated sulfuric acid in order to get any considerable

quantity of barium sulfate into solution, and dilution with water causes reprecipitation of barium sulfate:

$$BaSO_4 + H_2SO_4 \rightleftarrows Ba(HSO_4)_2.$$

Barium sulfate is partially converted, as a result of the mass-action effect, into more soluble barium carbonate by boiling with a concentrated solution of sodium carbonate:

$$BaSO_4 + Na_2CO_3 \rightleftarrows BaCO_3 + Na_2SO_4.$$

To make this decomposition quantitative, the barium sulfate must be boiled with the sodium carbonate solution, filtered, treated with a new portion of sodium carbonate solution, and the process repeated until the filtrate no longer gives a test for sulfate. The more concentrated the sodium carbonate solution is, the more complete will be the decomposition. The highest degree of concentration will be reached by *fusion of the barium sulfate with anhydrous sodium carbonate.*

Consequently, to obtain a solution of barium ions from insoluble barium sulfate, it is best to proceed as follows: Mix the solid with four to six times as much anhydrous sodium carbonate and fuse the mixture in a platinum crucible. Cool, boil the residue with a little water until thoroughly disintegrated, and filter. Wash the residue with hot, normal sodium carbonate solution, until the filtrate gives no test for sulfate ions, and then with a little water. Dissolve the residue of barium carbonate in dilute hydrochloric, nitric or acetic acid.

If the product of the fusion were treated with considerable water, or if the residue were washed at once with considerable hot water, the dissolved sodium sulfate would react with the insoluble barium carbonate to form less soluble barium sulfate. This is prevented, in accordance with the mass-action principle, by keeping the concentration of the sodium carbonate sufficiently large.

6. **Fluosilicic Acid** produces a white, crystalline precipitate of barium fluosilicate:

$$H_2SiF_6 + BaCl_2 = 2\,HCl + BaSiF_6.$$

In order to effect complete precipitation, the solution must stand some time. Barium fluosilicate is difficultly soluble in water and dilute acids, and insoluble in alcohol.

7. **Absolute Alcohol** dissolves neither the nitrate nor the chloride; neither of these salts is deliquescent. 100 cc. 66 per cent alcohol (by volume) dissolve 3.3 gms. of $BaCl_2 \cdot 2\,H_2O$.

8. **Concentrated Hydrochloric Acid** and **Nitric Acid** will precipitate from fairly-concentrated barium solutions the chloride and nitrate respectively.

9. **Sodium Phosphate** produces a white precipitate of barium phosphate in neutral or alkaline solutions of barium salts as with calcium

and strontium salts. According to Fresenius, $BaHPO_4$ is converted only partially into $Ba_3(PO_4)_2$ upon adding ammonium hydroxide.

10. **Potassium Ferrocyanide** added to a concentrated solution of a barium salt gives a white, crystalline precipitate of barium-potassium ferrocyanide, $BaK_2[Fe(CN)_6] \cdot 3\,H_2O$. In the presence of ammonium salts, the composition of the precipitate varies. The precipitate is more soluble than the corresponding calcium salt.

11. **Sodium Sulfite** gives a white precipitate of barium sulfite, $BaSO_3$, which is not very soluble in dilute acetic or very dilute hydrochloric acid.

Reactions in the Dry Way

Heated with sodium carbonate on charcoal before the blowpipe, the barium compounds, unlike those of calcium and strontium, do not give a brightly luminous mass, because the barium carbonate formed is not decomposed at this temperature into the infusible oxide and carbon dioxide, but merely sinters together somewhat. Volatile barium salts color the non-luminous gas flame yellowish-green. The sulfate is only slightly volatile in the hottest flame, and in the ordinary gas flame it shows scarcely any coloration. In order to obtain the coloration, it is best to change the sulfate into chloride, by reducing a small particle on a platinum wire in the upper reducing flame to sulfide and adding a little hydrochloric acid by means of a capillary tube. The wire on then being brought into the flame will give the characteristic flame coloration.

Flame Spectrum. — A number of deep green lines, weaker lines in the orange-yellow part of the spectrum, and one blue line.

Orange-yellow (654.0 $\mu\mu$, 629.8 $\mu\mu$), (624.0 $\mu\mu$, 617.9 $\mu\mu$, 610.9 $\mu\mu$, 603.2 $\mu\mu$). Yellow 528.5, yellow triple line (576.9 $\mu\mu$, 572 $\mu\mu$, 564.8 $\mu\mu$). Green 553.5 $\mu\mu$, 534.7 $\mu\mu$, 524.3 $\mu\mu$, 513.7 $\mu\mu$, 500.0 $\mu\mu$. Blue 484.7 $\mu\mu$.

Separation of Calcium, Strontium, and Barium

In the course of a systematic analysis these three metals are always obtained in the form of their insoluble carbonates, either by precipitation with ammonium carbonate from fairly dilute solution in the presence of ammonium chloride (cf. p. 109) or by fusion of the sulfates with sodium carbonate.

A number of excellent methods have been proposed for the analysis of the alkaline earth group. The characteristic reactions of barium, strontium and calcium are so similar that difficulties are likely to arise in any scheme whenever a small quantity of one of these elements is present together with a large quantity of another; thus a precipitate

caused by the presence of much strontium may be confused with one produced by a little barium. Three methods of analyzing the group will be described.

TABLE IV. — ANALYSIS OF GROUP IV

METHOD A

Solution may contain: Ba++, Sr++, Ca++, Mg++, K+, Na+, NH_4+. *Add NH_4OH and $(NH_4)_2CO_3$. Examine filtrate for Mg, K, Na according to Table I, II or III, pp. 101–5.* (1). *Dissolve carbonates of Ba, Sr and Ca, in 2-normal HNO_3. Evaporate to dryness. Dissolve a part of the residue in a little water and add $CaSO_4$ solution* (2); *(a) no precipitate is formed. Ca is present* (3); *(b) a precipitate forms slowly, Sr is present and possibly Ca* (4); *(c) a precipitate is formed at once, Ba is present and possibly Sr and Ca* (5). *Treat the remainder of the dry residue with C_2H_5OH* (6).

Residue: $Sr(NO_3)_2$, $Ba(NO_3)_2$. *Heat with solid NH_4Cl* (8). *Treat cold residue with C_2H_5OH.*		Solution: $Ca(NO_3)_2$. *Evaporate to dryness and test in the flame.* Brick-red coloration shows *Ca.* (7)
Residue: $BaCl_2$. *Test in the flame. Dissolve in water, heat to boiling* and *add $HC_2H_3O_2$ and K_2CrO_4,* yellow precipitate of $BaCrO_4$ shows *Ba.* (9)	Solution: $SrCl_2$. *Evaporate to dryness and test in flame.* Carmine-red coloration shows *Sr.* (9)	

PROCEDURE

1. Concentrate the filtrate from Group III to small volume in a porcelain dish, add 6-normal HCl to acid reaction and filter if the solution is not perfectly clear. If sulfur runs through the filter paper, make a pulp by shaking small pieces of filter paper in a bottle with water, add some of this pulp to the turbid solution, stir or shake, and filter. Wash the residue till the volume of the filtrate is about 50 cc., heat this solution to boiling, add NH_4OH and $(NH_4)_2CO_3$. Filter and examine the filtrate for Mg++, K+ and Na+. The precipitate may contain $BaCO_3$, $SrCO_3$ and $CaCO_3$.

2. Dissolve the carbonates in dilute nitric acid and evaporate the solution in a small porcelain crucible just to dryness, by heating with a small flame kept in constant motion and heating very carefully until all the moisture and nitric acid have been expelled. Take care not to overheat the residue, as this will cause the conversion of the nitrates to oxides. Dissolve a small portion of the residue in as little water as possible and add 5 cc. of calcium sulfate solution.

3. If *no precipitate* is formed, only calcium (and magnesium) can be present.

4. If a *precipitate forms only after standing some time*, barium is absent, strontium is present and calcium may be present.

5. If a *precipitate forms immediately*, barium is present and possibly the other members of the group as well. This preliminary test with calcium sulfate solution is very useful. It must be remembered in making this test that 5 cc. of saturated calcium sulfate solution contain only 3 mg. of calcium ions so that a large precipitate cannot be obtained with this reagent even when much barium is present; 10 mgs. of barium will give the maximum possible precipitate with 5 cc. of calcium sulfate reagent.

6. Treat the remaining residue, which must be perfectly dry, with a little absolute alcohol, stir with a glass rod and pour the alcohol through a filter which has been wet with absolute alcohol, catching the filtrate in a small porcelain crucible. If any calcium was present in the original residue of nitrates, some of it will have been dissolved by the alcohol.

7. Evaporate the alcoholic solution to dryness, wipe out the crucible with a piece of filter paper containing no calcium, fold the paper and fasten it to a platinum wire. Burn the paper, moisten the ash with hydrochloric acid and hold it in the non-luminous flame. The presence of *calcium is shown by a brick-red flame coloration.*

8. If calcium is found to be present, repeat the treatment of the original nitrate residue with absolute alcohol several times to dissolve out all the calcium nitrate. Then mix the remaining residue with an excess of ammonium chloride and heat until no more ammonium fumes are evolved. By this operation the nitrates are converted to chlorides. The nitrogen, which has a negative polarity of three in ammonium chloride (having four negative valences and one positive) is oxidized by the quinquevalent, positively-charged nitrogen of the nitrate and the product of this oxidation and reduction is nitrogen. At the same time the negatively-charged chlorine is oxidized by the nitrogen of the nitrate, forming free chlorine and nitric oxide, the latter escaping partly as such and partly oxidizing the nitrogen of the ammonium. The oxidation of ammonium chloride requires four positive charges of electricity; the nitrogen of the strontium nitrate loses five positive charges if reduced to nitrogen and three if reduced to NO. Assuming a complete reduction to nitrogen, the equation is

$$2\,Sr(NO_3)_2 + 6\,NH_4Cl = 2\,SrCl_2 + 5\,N_2\uparrow + Cl_2\uparrow + 12\,H_2O;$$

assuming the nitrate reduced only to nitric oxide, NO.

$$Sr(NO_3)_2 + 2\,NH_4Cl = SrCl_2 + 4\,H_2O + 2\,NO\uparrow + N_2\uparrow.$$

It is also easy to change the nitrate to chloride by evaporation with concentrated hydrochloric acid (cf. p. 60).

9. Treat the residue of chlorides with a little 66 per cent alcohol (by volume) exactly as described above and test the alcohol solution for strontium by the flame test; a *carmine-red coloration shows the presence of strontium.* Wash any residual chloride with 80 per cent alcohol to dissolve out all the strontium chloride and test the residue likewise in the flame for barium; *a yellowish-green coloration shows barium.* If there is sufficient residue, dissolve it in a little water and a little acetic acid, heat to boiling and test for barium with potassium chromate solution; a yellow precipitate at this stage of the analysis is positive proof of the presence of barium.

The above method of analysis is based on the assumption that the alkaline-earth carbonates were formed under conditions such that only barium, strontium and calcium are present in the carbonate residue or precipitate. If the ammonium carbonate is added under the conditions described on p. 104, the magnesium will be precipitated as carbonate, together with calcium, strontium and barium. The following method of analyzing this group has been tested thoroughly by A. A. Noyes *

* A course of Instruction in the Qualitative Analysis of Inorganic Substances.

and his students and permits the identification of as little as 1 mg. of any constituent in the presence of 500 mgs. of any other member of the group.

TABLE V. — ANALYSIS OF GROUP IV

METHOD B

Solution may contain: Ba++, Sr++, Mg++, K+, Na+, NH_4+. *Concentrate to 10 cc.; add 15 cc. $(NH_4)_2CO_3$ reagent, or more if necessary, and an equal volume of C_2H_5OH. Stir, let stand 30 minutes and filter. Test filtrate for Na+ and K+ according to Table II, p. 104. Dissolve the precipitate, which may contain $BaCO_3$, $SrCO_3$, $CaCO_3$ and $MgCO_3 \cdot (NH_3)_2CO_3 \cdot 4H_2O$, in 6-normal $HC_2H_3O_2$, add $NH_4C_2H_3O_2$ and K_2CrO_4.* (1)

Precipitate: $BaCrO_4$. *Dissolve in HCl. Evaporate to dryness. Test residue in flame, treat with 3 cc. of 6-normal $HC_2H_3O_2$, 20 cc. of 3-normal $NH_4C_2H_3O_2$ and 15 cc. of water. Heat to boiling and test with K_2CrO_4 solution.* Yellow precipitate is $BaCrO_4$. (2)	Filtrate: Sr++, Ca++, Mg++. *Add NH_4OH. Dilute to 65 cc. and add 50 cc. C_2H_5OH. Shake the solution with filter paper pulp and filter.* (3)		
	Precipitate: $SrCrO_4$. *Boil with $(NH_4)_2CO_3$ and $K_2C_2O_4$. Filter and reject the filtrate. Dissolve residue in 5 cc. of normal $HC_2H_3O_2$ and add 2 cc. of normal Na_2SO_4 solution.* White precipitate of $SrSO_4$ shows Sr is present. (4)	*Dilute with 50 cc. of water, add 3 cc. of 3-normal $K_2C_2O_4$. If a precipitate forms, add more $K_2C_2O_4$ if necessary, heat and filter.* (5)	
		Precipitate: CaC_2O_4. *Dissolve in 5 cc. of 6-normal H_2SO_4 and add 20 drops of C_2H_5OH.* White precipitate is $CaSO_4$. (5)	Filtrate: Mg++. *Add NH_4OH and Na_2HPO_4. Dissolve in 5 cc. of 2-normal H_2SO_4, add 10 cc. C_2H_5OH and filter if necessary. Add NH_4OH and Na_2HPO_4.* Precipitate is $MgNH_4PO_4$. (6)

PROCEDURE

1. Evaporate the filtrate from Group III till salts crystallize out, dilute to 10 cc. if necessary, and filter off sulfur and ammonium salts. Add to the filtrate 15 cc. of 9-normal $(NH_4)_2CO_3$ reagent and 15 cc. of C_2H_5OH. If a large precipitate results add 15 cc. more of these two reagents. Shake well and allow to stand, with occasional shaking, for half an hour. Filter and wash with a little of the ammonium carbonate reagent. The filtrate contains the alkali ions.

Dissolve the precipitated carbonates by pouring small portions of hot acetic acid through the filter and evaporate the resulting solution to dryness without overheating the residue. Moisten the residue with 2 cc. of 6-normal $HC_2H_3O_2$, 10 cc. of 3-normal $NH_4C_2H_3O_2$ and 10 cc. of water. Heat to boiling and precipitate the barium as chromate by adding hot 3-normal K_2CrO_4 solution, drop by drop, until no further precipitation takes place and the solution is decidedly yellow in color. Boil gently for about two minutes longer and filter through paper capable of holding very fine crystals.

2. If a considerable precipitate of strontium carbonate is obtained by the procedure given in § 3 below, it is possible that a *small* precipitate of chromate obtained in (1) may be strontium chromate and it is then necessary to try a confirmatory

test for barium. Pour through the filter containing the chromate precipitate repeatedly, 5 cc. of hot, 6-normal HCl and evaporate the solution just to dryness. Treat the residue with acetic acid, ammonium acetate and potassium chromate solutions exactly as in (1). If a yellow chromate precipitate is obtained again, barium is present.

3. To precipitate the strontium, add NH_4OH to the filtrate from (1) till the color of the solution changes from orange to yellow and then add 5 cc. more. Heat to about 65° and add 15 cc. of alcohol in 5 cc. portions, shaking 15 seconds after each addition. Cool and allow to stand at least 5 minutes. If considerable strontium chromate is formed, add 5 cc. more of potassium chromate solution and 15 cc. of alcohol. Filter with suction but do not wash the precipitate. Place the filtrate aside for the calcium and magnesium tests (§ 5).

4. Pour repeatedly through the filter containing the strontium chromate precipitate a 10 cc. portion of boiling-hot water. Add exactly 1 cc. of 3-normal Na_2CO_3 solution and 12 cc. of 3-normal $K_2C_2O_4$ and boil gently for 5 minutes in a covered casserole. Filter while hot and reject the filtrate. The precipitate will contain the strontium as carbonate and any contaminating calcium will be present as oxalate. Wash the precipitate thoroughly with water and dissolve the carbonate in 5 cc. of cold, normal $HC_2H_3O_2$. To the solution add 2 cc. of normal sodium sulfate solution, heat to boiling and allow to stand 10 minutes. A white precipitate of strontium sulfate shows the presence of strontium.

5. Dilute the ammoniacal filtrate from (3) with 50 cc. of water, add just 3 cc. of 3-normal $K_2C_2O_4$ solution and allow the mixture to stand at least 15 minutes. If there is no precipitate of calcium oxalate formed, pass on to (6).

If a precipitate is obtained, heat the mixture to boiling and add 3–10 cc. more of the $K_2C_2O_4$ reagent, according to the size of the carbonate precipitate obtained in (1). Heat 5 minutes, filter and wash with hot water. Test the filtrate for magnesium according to (6). Treat the precipitate, or a small portion of it, with 5 cc. of 6-normal H_2SO_4 to which 20 drops of alcohol have been added. Add 10 cc. more of alcohol and let the mixture stand for several minutes. A white precipitate of calcium sulfate shows the presence of calcium.

6. To test for magnesium ions, add 15 cc. of 15-normal NH_4OH and 25 cc. of normal Na_2HPO_4 to the filtrate from the $K_2C_2O_4$ treatment (5). Cool, shake and allow to stand at least 30 minutes. Filter, reject the filtrate and wash the precipitate once with alcohol. To confirm the magnesium, dissolve the precipitate in 5 cc. of 2 N sulfuric acid, add 20 cc. of alcohol and stir well for two or three minutes. Filter off any calcium sulfate that may form, and repeat the precipitation of the magnesium as phosphate (cf. p. 102).

COMPARATIVE SOLUBILITIES OF ALKALINE-EARTH SALTS

The numbers in the table show the solubility in milli-equivalents per liter at 20°. The letters v.s. (very soluble) denote more than 1 equivalent per liter.

	Mg	Ca	Sr	Ba
Sulfate	v.s.	30	1.5	0.02
Chromate	v.s.	60	12.	0.03
Carbonate	20.	0.2	0.2	0.2
Hydroxide	0.3	45.	130.	450.
Fluoride	3.8	0.4	1.9	18.
Oxalate	5.0	0.09	0.5	0.8

TABLE VI. — ANALYSIS OF GROUP IV

METHOD C

Solution may contain: Ba^{++}, Sr^{++}, Ca^{++}, Mg^{++}, Na^{+}, K, NH_4^{+}. *Add NH_4OH and $(NH_4)_2CO_3$. Filter and examine filtrate as in Method A p. 118. Dissolve carbonates of Ba, Sr and Ca in hot, dilute $HC_2H_3O_2$ and add $NH_4C_2H_3O_2$ and K_2CrO_4.* (1)

Precipitate: $BaCrO_4$. *Dissolve in HCl, evaporate to dryness and test in the flame.* Green color shows Ba is present. (2)	Filtrate: Sr^{++}, Ca^{++}. *Add $(NH_4)_2CO_3$ to reprecipitate the carbonates. Dissolve carbonates in dilute HCl, boil off CO_2; add NH_4OH and $K_4[Fe(CN)_6]$.* (3)

Precipitate: $CaK_2Fe(CN)_6$.	Filtrate: *Add $(NH_4)_2CO_3$.* A white precipitate of $SrCO_3$ shows Sr is present. (4)

PROCEDURE

1. Proceed as in Method A (1), but dissolve the precipitated carbonates in hot, dilute acetic acid. Evaporate the solution nearly to dryness, in order to remove the excess acid, dilute with water to a volume of about 25 cc. and filter if necessary. Heat to boiling, add two or three drops of acetic acid if necessary, and potassium chromate solution enough to color the solution yellow. If the solution smells of acetic acid, add a little more potassium chromate. After an hour examine carefully to see whether any precipitate of $BaCrO_4$ has formed. If this is the case, filter and examine the filtrate for calcium and strontium as described in § 3. In case a small precipitate is formed it may be due to strontium. To confirm the barium test, dissolve the $BaCrO_4$ in 5 cc. of hot HCl, evaporate to dryness in a small porcelain dish and test with the flame with the aid of a clean platinum wire, which is first moistened with HCl and heated in the flame until no coloration is obtained.

3. To the filtrate from the K_2CrO_4 precipitation, add $(NH_4)_2CO_3$ solution, heat nearly to boiling and allow to stand at least 10 minutes. Filter and wash the precipitate with a little hot water. Dissolve the precipitate in a *little* dilute HCl, make alkaline with NH_4OH, heat to boiling, add concentrated $K_4[Fe(CN)_6]$ solution and again heat. If a precipitate forms, showing the presence of calcium, filter and test the filtrate for strontium.

4. Add, if necessary, a little more $K_4Fe(CN)_6$ to make sure that all calcium was precipitated. Then add $(NH_4)_2CO_3$ and allow the solution to stand for some time. This should be $SrCO_3$. In case the precipitate is very small test it in the flame as in the barium test. A bright red coloration shows the presence of strontium.

Traces of alkalies and *alkaline earths* are recognized best by means of the spectroscope. At this place, therefore, a brief description of spectroscopic analysis will be given.

Spectroscopic Analysis (Bunsen and Kirchhoff, 1865)

If a ray of white light is passed through a glass prism, not only is the direction of the ray changed, but the white light is decomposed into colors; it suffers dispersion. It will be found that the red rays

are deflected least, while the violet rays are deflected most. The picture obtained — the spectrum — if projected on a screen (Fig. 5), does not show the colors sharply separated, but merging into one another. Such a spectrum is called a continuous, or uninterrupted, spectrum. *Every glowing solid or liquid body emits white light; the spectra obtained in all such cases will be continuous ones.* Glowing vapors and gases behave quite differently. They do not emit white light, but light composed of rays of definite wave lengths, which are characteristic for each gas and for each vapor. The light emitted from glowing vapors or gases, when decomposed by the prism, yields on the screen a *discontinuous* or *interrupted spectrum.* If the light is passed through a fine slit before reaching the prism, the spectrum will be found to consist of a greater or less number of colored lines which always appear in the same place with any given substance, provided the prism or its position is not changed. In order to determine the

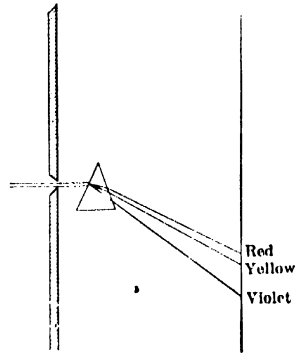

FIG. 5

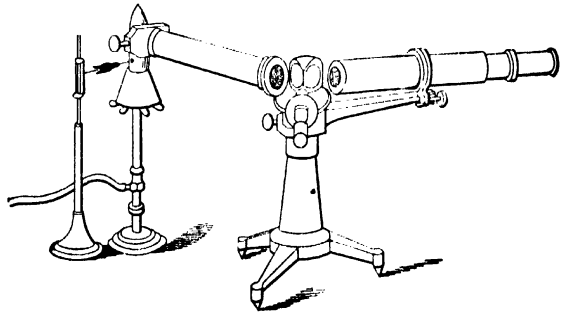

FIG. 6

exact position of these lines, we make use of the spectroscope of Bunsen and Kirchhoff (Fig. 6). Fig. 7 shows a cross-section of the apparatus.

The substance to be examined is placed in the loop of a platinum wire and introduced at *A* into the non-luminous gas flame, by means of which it is volatilized. The rays of light pass through the slit

into the tube Sp, reach the prism, by which the rays are refracted into the telescope C (the collimator) and are observed at D. Upon a glass plate at the end of the tube Sk is a transparent scale, which is

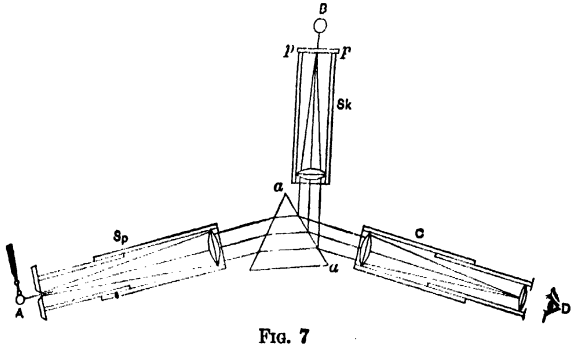

FIG. 7

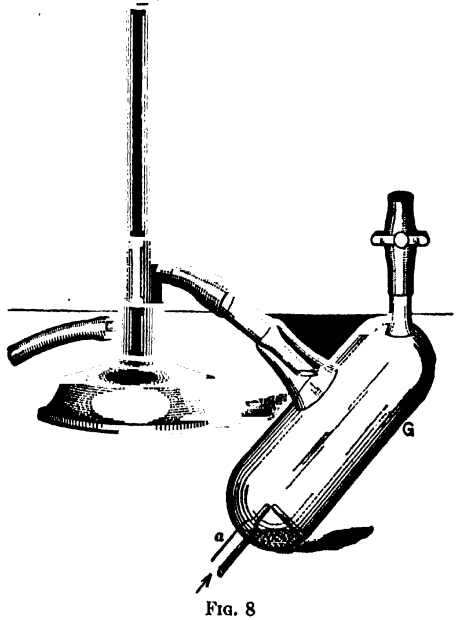

FIG. 8

illuminated by a small flame at *B*. This tube is so inclined toward the face *aa* of the prism that the rays of light from this tube are totally reflected into the tube *C*, and reach the eye of the observer; thus the

rays from the substance appear at a certain position on the scale. As, however, the position of the lines depends upon the dispersive power of the prism, and upon its angle of refraction, it is clear that the position of the lines will be somewhat different in different spectroscopes. As every ray has a definite wave length, it is better to give the wave lengths of the rays which appear, rather than their position on the scale.

Wave lengths are expressed in millionths of a millimeter, called micromillimeters, and designated as $\mu\mu$.

The following values for the wave lengths of the various lines in the spectrum are taken from the most accurate measurements:

Red rubidium line	Rb_δ	= 795.0 $\mu\mu$
rubidium line	Rb_γ	= 781.1 $\mu\mu$
potassium double line	K_α	= 766.9 $\mu\mu$ = 766.5 $\mu\mu$
lithium line	Li_α	= 670.8 $\mu\mu$
cadmium line *	Cd_γ	= 643.9 $\mu\mu$
Orange-yellow lithium line	Li_β	= 610.8 $\mu\mu$
Yellow sodium (middle of the double line)	Na	= 589.3 $\mu\mu$
Green calcium line	Ca_β	= 554.4 $\mu\mu$
thallium line	Tl	= 535.0 $\mu\mu$
cadmium line *	Cd_α	= 508.6 $\mu\mu$
Blue cadmium line *	Cd_β	= 480.0 $\mu\mu$
cadmium line *	Cd_γ	= 467.8 $\mu\mu$
strontium line	Sr_δ	= 460.7 $\mu\mu$
cesium line	Cs_β	= 459.3 $\mu\mu$
cesium line	Cs_α	= 455.5 $\mu\mu$
Blue-violet indium line	In_α	= 451.1 $\mu\mu$
Violet rubidium line	Rb_β	= 421.5 $\mu\mu$
rubidium line	Rb_α	= 420.2 $\mu\mu$
indium line	In_β	= 410.1 $\mu\mu$
potassium line	K_β	= 404.4 $\mu\mu$
H (Frauenhofer C line)		= 396.8 $\mu\mu$

Let us assume that the foregoing lines were observed at the following positions on the scale: K_α at 17, K_β at 154, Li_α at 32, Na at 50, Tl at 68, Sr_δ at 101, In_α at 111, and In_β at 149.

If now, upon a rectangular system of coördinates, we plot the wave lengths as ordinates and the corresponding scale divisions as abscissas,

* The cadmium lines can be seen distinctly only in spark spectra.

and connect the points of intersection, we shall get a curve * which expresses the relation between the wave lengths and the corresponding divisions on the scale (Fig. 9). We can, without serious error, regard the portions of the curve between two points of intersection as proportional to the corresponding scale divisions.

The use of the curve may be illustrated by a single example:

Suppose we observe at the division 60 of the scale a line x. What is the corresponding wave length? The line lies between the sodium and thallium lines, which are of known wave lengths.

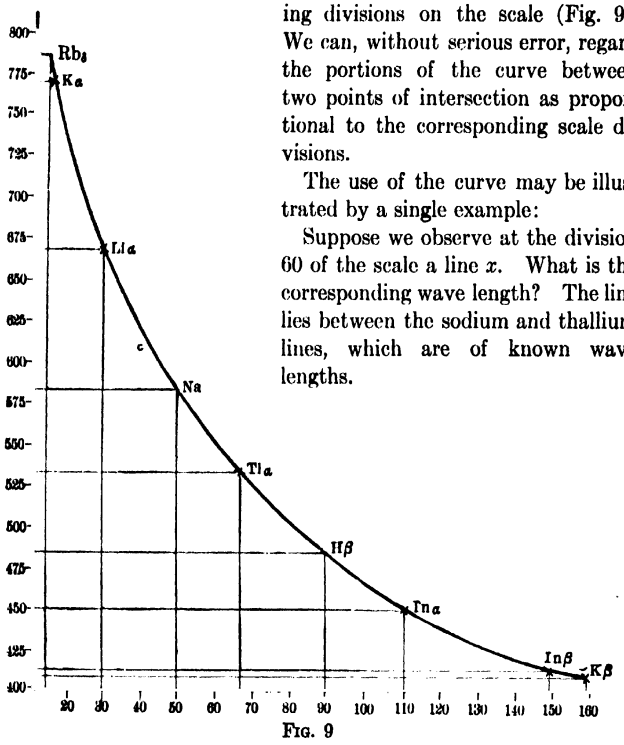

FIG. 9

The sodium line lies at division 50 and corresponds to 589.3 $\mu\mu$
The thallium line " 68 " 535.0 $\mu\mu$
Consequently 18 scale divisions = 54.3 $\mu\mu$
and 1 scale division = 3.017 $\mu\mu$

The line x is at 60 = 50 + 10 divisions, and these correspond to

Division 50 = 589.30 $\mu\mu$
10 divisions = 30.17 $\mu\mu$
Division 60 = 559.13 $\mu\mu$

* The curve is ordinarily drawn only for wave lengths lying between 800–400 $\mu\mu$ because only these light rays are visible to the eye. The rays of shorter wave length than 400 $\mu\mu$ are called *ultra-violet rays* and those longer than 800 $\mu\mu$ are known as ultra-red rays. The former can be detected by their action upon photographic plates, and the latter by their thermic effect or by their action upon specially prepared photographic plates.

The scale divisions increase in their value as the wave lengths diminish, so that we subtract the 30.17 from 589.3.

The spectra obtained as described above are very beautiful, but usually of short duration. More permanent spectra may be obtained with the aid of the Beckmann burner,* Fig. 8, p. 124. From one-half to 1 cc. of the salt solution to be tested is placed in the glass vessel *G*, the gas is lighted, and a good blast of air introduced at *a*. By means of the air current, a little of the solution is carried mechanically over into the burner in the form of spray, and thus the salt reaches the non-luminous flame. In this way it is possible to get a fairly permanent spectrum by the use of only a few milligrams of substance. There is then plenty of time to make the measurements without having to stop and replenish the sample.

Measuring the Lines and Bands of the Spectrum

The correctness of a curve of wave lengths, prepared as just described, depends upon the accuracy with which the observed lines or bands are measured. To insure accuracy, all the better forms of

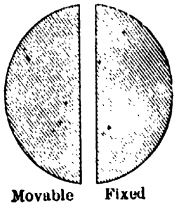

FIG. 10. — Position with unsymmetrical slit.

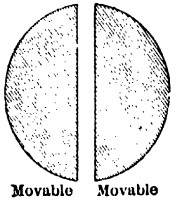

FIG. 11. — Position with symmetrical slit.

apparatus are provided with cross-hairs in the ocular, and the cross must each time be made to cover a definite part of the line to be measured. The choice of such position depends upon the construction of the slit at the end of the spectroscope. If the apparatus is provided with an unsymmetrical slit, i.e., one of which only one side is movable while the other remains in a fixed position, then the reading should be made with the cross-hairs coinciding with the edge of the band on the immovable side of the slit. Such a position is shown in Fig. 10, i

* Cf. *Z. phys. Chem.*, **11**, 472.

which it is assumed that the right-hand side of the slit is immovab

In the case of a symmetrical slit, i.e., one in which both sides the slit open and close symmetrically, the cross-hairs must be made t meet in the center of the line to be measured (Fig. 11).

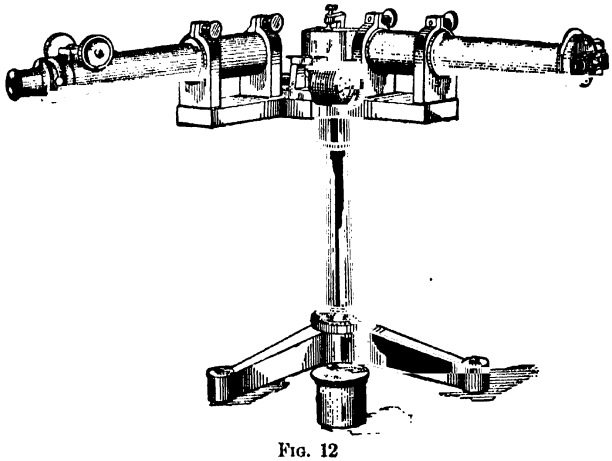

FIG. 12

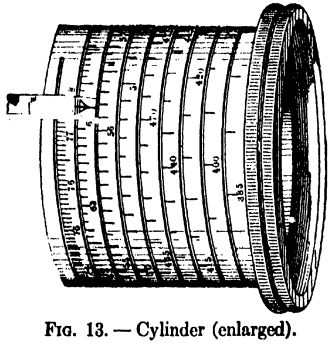

FIG. 13. — Cylinder (enlarged).

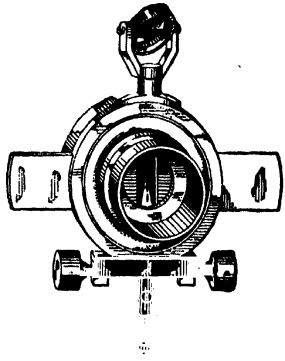

FIG. 14. — Ocular with steel point and mirror.

The measurements can be made more readily and more accurately by the aid of Hilger's Wave Length Spectroscope (Fig. 12). In this apparatus the telescope and collimator are both fixed in position, but the prism can be rotated by means of a cylinder upon which is engraved a very exact wave-length curve (Fig. 13). The pointer of the cylinder gives the desired wave length with an accuracy of $\pm 0.2\ \mu\mu$.

For the rapid adjustment of the apparatus, the ocular shown in Fig. 14 is convenient. In this ocular there is a very fine, polished steel point beneath the cross-hairs; it is lighted from the outside by means of a small mirror so that it is seen very distinctly. This point is made to coincide with the desired edge, or the middle of the line, and then only the final adjustment is made with the cross-hairs.

It is not possible to volatilize all substances in the gas flame. The non-volatile substances will not give any flame spectra, but by means of the electric spark they will be volatilized enough to give spark spectra. As the determination of their spark spectra furnishes the only method by which the purity of many substances may be tested, the methods for the production of spark spectra will be outlined briefly.

The apparatus invented by Bunsen consists of two platinum wires which are each attached at one end to conical pieces of charcoal. The latter are soaked with a solution of the substance to be tested. The two carbon points are now placed opposite to one another, quite near together, and the other ends of the platinum wires are connected with an induction coil, which causes sparks to pass between the two carbon points, volatilizing some of the salt. If now the sparks are viewed through a spectroscope, a large number of lines will be seen, of which only a part are produced by the substance itself. Some of the lines are caused by the carbon points and some by the air. In order to determine which lines are caused by the substance that is being tested, the experiment is first performed without using any of the substance, and the spectrum thus obtained is either drawn or photographed. The experiment is then performed with some of the salt impregnated in the carbon points and the new lines in the spectrum will be caused by the substance.

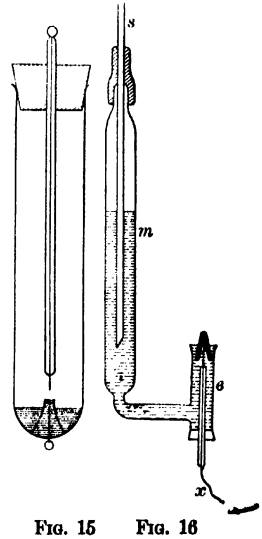

Fig. 15 Fig. 16

Spark spectra can be more conveniently produced by means of the so-called "fulgurator" of Delachanel and Mermet, as shown in Fig. 15. The salt solution is in a test-tube, so that the slit of the spectroscope cannot be contaminated with the spattered particles of the salt.

The small apparatus of H. Dennis, Fig. 16, is also very convenient for producing spark spectra. The platinum wire x is fused in a glass

tube and ends in a point of Ceylon graphite, which extends up out of the arm e of the apparatus. The upper pole is not shown in the illustration.

To fill the tube *m* with the salt solution of the substance to be tested, *s* is taken away, and the apparatus is inclined to the left. The solution is poured in at the upper end of *m*, when *s* is again introduced and shoved down until it reaches nearly to the bottom. The apparatus is now placed in a vertical position, whereby the liquid in *e* rises until it is level with the lower end of *s*. On raising *s* the liquid will rise to the upper edge of *e*. By means of electric sparks from the carbon point, enough of the liquid is evaporated to give the desired spectrum. Care should be taken to prevent any spattering of the substance into the slit of the spectroscope.

A far better fulgurator has been devised by E. H. Riesenfeld and G. Pfützer.* As anode the solution of the salt itself is used, as cathode a thin iridium wire which almost touches the surface of the liquid. If an electric arc is produced between such electrodes, nearly pure spectra are obtained without lines from the atmosphere. In this way even the magnesium lines can be identified. By flame spectra with the Bunsen burner only 0.2 mg. Ca, 0.6 mg. Sr and 14 mgs. Ba can be detected with certainty, but with this fulgurator 0.002 mg. Ca, 0.03 mg. Sr and 0.006 mg. Ba can be detected when present in 1 cc. of water.

To examine gas spectra, small Geissler tubes are used which contain the gas to be detected in a dilute condition. Besides flame spectra and spark spectra, there remain absorption spectra to be mentioned. If white light is passed through a colored solution or gas, certain rays are absorbed by the liquid, so that if the light is now examined in the spectroscope, these rays will be found to be lacking. We see a bright spectrum broken by black bands (absorption bands) which are characteristic for different substances. Thus solutions of permanganic acid, neodymium, praseodymium, erbium, and many other substances give characteristic absorption spectra. These absorption spectra are often obtained from colorless solutions.

It is to be noted that an absorption spectrum is often of quite different appearance according to whether the solution is dilute or concentrated. In measuring absorption bands the solution should be diluted with solvent until the band appears in the form of as fine a line as possible at the intersection of the cross-hairs, and further dilution should cause the disappearance of the band.

The same end is easily attained if, as R. Philip has suggested, the concentrated solution is placed in a test-tube and covered with more

* *Ber.*, **1913**, 3140.

of the solvent. The lowest layer then gives the spectrum of the concentrated solution and it becomes more and more dilute in the upper portions.

In order to obtain any of the above spectra sharply defined, it is necessary to have the spectroscope properly adjusted, i.e., the rays must come parallel from the collimator tube into the telescope. The telescope is removed and adjusted for parallel rays by focusing it upon some distant object. It is then replaced, the prism removed, and the collimator tube brought exactly opposite the telescope, so that the slit of the former can be observed by the latter. The collimator tube must be lengthened or shortened until the picture of the slit is sharply defined. The prism is now replaced and the scale tube adjusted until the scale also can be seen clearly defined. The instrument is now ready for use.

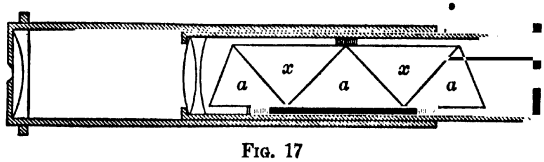

FIG. 17

The direct-vision pocket spectroscope, with an arrangement of prisms as shown in Fig. 17, is very convenient for ordinary use.

If it is desired to photograph a spectrum, the telescope tube is replaced by a camera as shown in Fig. 18. Such an apparatus is

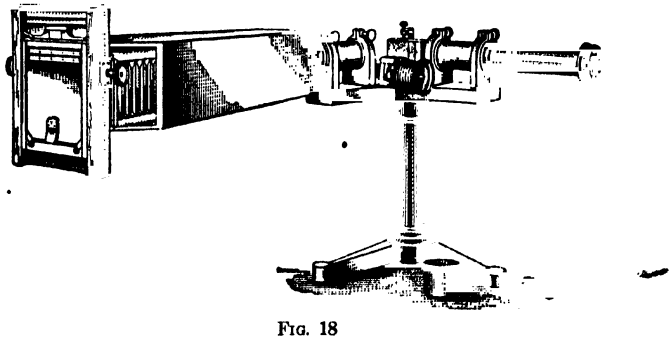

FIG. 18

called the *spectrograph*. With glass prism and glass objective lens, the spectrum can be photographed to about 350 $\mu\mu$. To make the ultra-violet part of the spectrum visible, the objective lens and the prism must be made of quartz and fluorspar, whereby it is possible to

photograph light rays of about 200 $\mu\mu$. For observing rays of still shorter wave length, fluorspar alone is requisite, as it absorbs the ultra-violet rays to a less extent than quartz does.

To photograph the ultra-red rays, specially prepared plates, as discovered and prepared by W. Abney, are necessary.*

* For methods of quantitative spectrum analysis consult W. Hempel and R. L. von Klemperer, *Z. angew. Chem.*, **1910**, 1756.

GROUP III. AMMONIUM SULFIDE GROUP

ALUMINIUM, TITANIUM, CHROMIUM, IRON, URANIUM, ZINC, MANGANESE, NICKEL, COBALT

ALUMINIUM, Al. At. Wt. 27.1

Sp. Gr. 2.56–2.67. M. Pt. = 658.7° C.

Occurrence. — Aluminium occurs very extensively in nature, principally in the form of silicates, of which the feldspars and micas with their decomposition products are important examples:

Orthoclase (feldspar), $K_3Al_3(Si_3O_8)_3$; kaolin (decomposed feldspar), $H_4Al_2Si_2O_9$; muscovite (mica), $KH_2Al_3(SiO_4)_3$. Impure kaolin is called clay.

Among the most important minerals which contain aluminium may be mentioned cryolite, Na_3AlF_6; spinel, $MgAl_2O_4$, or magnesium aluminate, which crystallizes in the regular system and is isomorphous with magnetite, $Fe \cdot Fe_2O_4$, and chromite, $Fe \cdot Cr_2O_4$; alunite, $KAl_3(SO_4)_2(OH)_6$; aluminium hydroxide as hydrargillite, $Al(OH)_3$, monoclinic; bauxite, $H_4Al_2O_5$, and diaspore, $HAlO_2$, orthorhombic.

Corundum, Al_2O_3, is next to the diamond the hardest mineral. Pure, transparent corundum often has a beautiful color and is classed with the precious stones. Thus the ruby, sapphire, oriental emerald, oriental topaz and amethyst are nearly pure corundum colored by a little foreign oxide. Emery is an intimate mixture of corundum, magnetite and iron sulfide. True topaz is $Al_2(F,OH)_2SiO_4$, turquoise is $Al_2(OH)_3PO_4 \cdot H_2O$, and garnet is chiefly $Ca_3Al_2(SiO_4)_3$.

Metallic aluminium is now made on a large scale by the electrolysis of Al_2O_3 dissolved in a bath of molten cryolite. It has a silver-white color and is only slightly attacked by exposure to the atmosphere. From the position of this element in the electromotive series (p. 41), the metal should be attacked readily by the atmosphere, and the reason it is apparently unattacked has been proved due to its becoming coated with a thin, firmly adherent, protective layer of oxide. Aluminium is trivalent in all its compounds; it forms only one oxide, Al_2O_3, which is amphoteric. The metal dissolves in acid to form an aluminium salt and in caustic alkali to form a soluble aluminate. Aluminium readily replaces the hydrogen of hydrochloric acid, but it dissolves less readily in dilute sulfuric acid and becomes passive when treated

with nitric acid. One theory of the cause of passivity is the formation of a closely adherent oxide film.

The action of aluminium upon dilute hydrochloric acid and upon aqueous solutions of caustic alkali is expressed by the following ionic equations:

$$2\,Al + 6\,H^+ \rightarrow 2\,Al^{+++} + 3\,H_2\uparrow,$$

$$2\,Al + 2\,OH^- + 2\,H_2O \rightarrow 2\,AlO_2^- + 3\,H_2\uparrow.$$

Aluminium salts are as a rule colorless, and those which are soluble in water show an acid reaction in aqueous solution, on account of their being hydrolyzed to a considerable extent. This explains the fact that on evaporating a solution of aluminium chloride in water we do not obtain aluminium chloride, but the insoluble oxide, or hydroxide:

$$AlCl_3 + 3\,HOH \rightleftarrows Al(OH)_3 + 3\,HCl.$$

The property which aluminium possesses of forming alums is very characteristic. The alums are double salts of aluminium sulfate with the sulfates of potassium, cæsium, rubidium, or ammonium, of the general formula $RAl(SO_4)_2 \cdot 12\,H_2O$, in which R represents one of the univalent metals just mentioned. Similar salts in which the aluminium is replaced by trivalent iron or chromium are also called alums. The alums crystallize in the regular system, usually in octahedrons. The common potassium alum is much less soluble in cold than in hot water. Thus 100 cc. of water dissolve 10.7 gms. of alum at 15° C. and 283 gms. at 100° C.

The sulfide of aluminium can be prepared only in the dry way. It is a pale-yellow substance, which is decomposed hydrolytically even by cold water into hydrogen sulfide and aluminium hydroxide:

$$Al_2S_3 + 6\,HOH = 3\,H_2S + 2\,Al(OH)_3.$$

Aluminium hydroxide is amphoteric; toward strong acids it plays the part of an alkali, toward strong bases it acts as an acid.

Reactions in the Wet Way

1. **Ammonia** produces a gelatinous precipitate of aluminium hydroxide, which, as a colloid, is somewhat soluble in water, but insoluble in the presence of ammonium salts:

$$AlCl_3 + 3\,NH_4OH = Al(OH)_3 + 3\,NH_4Cl.$$

The property which the aluminium hydroxide shows of partly dissolving in water, is common to all *colloidal* substances (cf. p. 58). When dissolved they are sometimes said to exist in the *hydrosole* condition and when precipitated as *hydrogele*.

The hydrosole form of aluminium hydroxide can be converted into

hydrogele *by the addition of salts,** preferably ammonium salts. *If, therefore, we desire to precipitate aluminium from a solution by means of ammonia, we take care that ammonium chloride is present.*

The freshly precipitated aluminium hydroxide is readily soluble in dilute acids; but after standing some time in a salt solution, or after long boiling, it becomes more difficultly soluble, so that it is necessary to digest it with acid for a long time in order to bring it completely into solution.

The solubility product of aluminium hydroxide is so small that it is precipitated by ammonia even in the presence of ammonium salt. Aluminium does not show a tendency to form soluble complex cations with ammonia.

2. **Potassium** or **Sodium Hydroxide** produces the same precipitate as ammonia, which is, however, in this case soluble in excess of the reagent, forming an alkali aluminate:

$$Al^{+++} + 3\,OH^- \rightarrow \mathbf{Al(OH)_3},$$
$$\mathbf{Al(OH)_3} + OH^- \rightarrow AlO_2^- + 2\,H_2O.$$

If dilute acid is added to a solution of an aluminate, there is formed at first a precipitate of aluminium hydroxide, which dissolves on further addition of acid:

$$AlO_2^- + H^+ + H_2O \rightarrow \mathbf{Al(OH)_3},$$
$$\mathbf{Al(OH)_3} + 3\,H^+ \rightarrow Al^{+++} + 3\,H_2O.$$

The aluminates are also decomposed by boiling with an ammonium salt,

$$AlO_2^- + NH_4^+ + H_2O \rightarrow \mathbf{Al(OH)_3} + NH_3\uparrow.$$

Aluminium hydroxide is soluble in neutral tartrates of the alkalies, so that in the presence of tartaric acid there will be no precipitation on the addition of ammonia. Consequently the aluminium is present in such a solution not as simple aluminium cations but chiefly as complex negative ions:

$$\mathbf{Al(OH)_3} + C_4H_4O_6^{--} \rightarrow C_4H_2(AlOH)O_6^{--} + 2\,H_2O.$$

Many other organic hydroxy-acids and hydroxy-compounds, such as malic and citric acids, sugars and starches, have the same effect of preventing the precipitation of aluminium hydroxide by ammonia.

3. **Ammonium Sulfide** causes precipitation of the hydroxide. When formed in the dry way, aluminium sulfide is completely hydrolyzed by water:

$$\mathbf{Al_2S_3} + 6\,HOH = \mathbf{2\,Al(OH)_3} + 3\,H_2S\uparrow.$$

* This principle is illustrated by the technical process of "salting out" colloidal dyes from their solutions.

The aqueous solution of ammonium sulfide is in equilibrium with NH_4OH and H_2S formed by hydrolysis. There are, therefore, enough OH^- ions in a solution of ammonium sulfide to cause the precipitation of $Al(OH)_3$.

4. **Alkali Carbonates** precipitate aluminium hydroxide (hydrolysis):

$$2\,Al^{+++} + 3\,CO_3^{--} + 3\,HOH \rightarrow \mathbf{2\,Al(OH)_3} + 3\,CO_2\uparrow.$$

5. **Barium Carbonate,** suspended in water and added to the solution of an aluminium salt, also precipitates the hydroxide:

$$2\,Al^{+++} + 3\,\mathbf{BaCO_3} + 3\,HOH \rightarrow 3\,Ba^{++} + 3\,CO_2\uparrow + \mathbf{2\,Al(OH)_3}.$$

6. **Alkali Acetates** produce no precipitation in cold neutral solutions, but, on boiling the solution, a very voluminous precipitate of basic *aluminium* acetate is formed:

$$Al^{+++} + 3\,C_2H_3O_2^- = \underset{\text{Soluble}}{Al(C_2H_3O_2)_3}\ \text{(in the cold)},$$

$$Al(C_2H_3O_2)_3 + 2\,HOH \rightleftarrows \mathbf{Al}\begin{matrix}\diagup\mathbf{OH}\\ -\mathbf{OH}\\ \diagdown\mathbf{C_2H_3O_2}\end{matrix} + 2\,HC_2H_3O_2\ \text{(on boiling)}.$$

If the solution is allowed to cool, the basic aluminium acetate redissolves. The reaction is, therefore, a reversible one, and goes more completely from left to right according as we increase the amount of water and raise the temperature (cf. pp. 51 and 52).

7. **Alkali Phosphates,** e.g., Na_2HPO_4, give a gelatinous precipitate of aluminium phosphate:

$$2\,HPO_4^{--} + Al^{+++} \rightarrow \mathbf{AlPO_4} + H_2PO_4^-,$$

or, on addition of ammonia,

$$HPO_4^{--} + NH_3 + Al^{+++} \rightarrow \mathbf{AlPO_4} + NH_4^+.$$

Aluminium phosphate is soluble in mineral acids, insoluble in acetic acid (differing from Ca, Sr, Ba, Mg), but readily soluble in sodium or potassium hydroxide solutions:

$$\mathbf{AlPO_4} + 4\,OH^- \rightarrow AlO_2^- + PO_4^{---} + 2\,H_2O.$$

On boiling this alkaline solution (obtained in the last reaction) with ammonium chloride, a precipitate will be formed, consisting of a mixture of aluminium phosphate and aluminium hydroxide; while barium chloride, on the contrary, will precipitate barium phosphate from such a solution and leave the aluminate dissolved.

8. **Sodium Thiosulfate,** $Na_2S_2O_3$, completely precipitates the aluminium as hydroxide on boiling:

$$2\,Al^{+++} + 3\,S_2O_3^{--} + 3\,HOH = \mathbf{3\,S} + 3\,SO_2\uparrow + \mathbf{2\,Al(OH)_3}.$$

The sodium thiosulfate, being a salt of a weak acid, serves to neutralize the H^+ ions formed by the hydrolysis of the aluminium salt, and the free $H_2S_2O_3$ is so unstable that it breaks down into S and SO_2; equilibrium is disturbed by the precipitation of the $Al(OH)_3$ and S and by the escape of SO_2 gas.

9. **Morin** in alcoholic solution shows a green fluorescence when brought in contact with only a trace of neutral aluminium salt. (This reaction is very sensitive.) Beryllium salts and salts of the rare earths do not give the test. Morin, $C_{13}H_8O_6 \cdot 2\,H_2O$ or $C_{15}H_{10}O_7 \cdot 2\,H_2O$, is the color principle of old fustic, a dyewood. Other organic dyestuffs give more or less characteristic color tests with aluminium. Thus Horsley and Schumacher-Kopp * recommend tincture of campêche wood, Luckow † uses cochineal, and Attack ‡ suggests alizarine.

Alizarine, $C_{14}H_6O_2(OH)_2$, in a freshly-prepared 0.01 per cent solution which is 0.6-normal in acetic acid and 3-normal in sodium acetate, gives a red or pink color when a little of it is added to a fresh precipitate of aluminium hydroxide. If a large precipitate is to be tested, shake a little of the precipitate with filter-paper pulp in a test tube and add about 3 cc. of the alizarine reagent.

10. **Ether** precipitates white, crystalline aluminium chloride, $AlCl_3 \cdot 6\,H_2O$, from a concentrated solution which is saturated with HCl gas. Aluminium may be separated from beryllium in this way.

11. **Oxalic Acid** and its salts do not form precipitates in solutions of aluminium salts. This helps to distinguish aluminium from certain rare earths of this analytical group (cerium, lanthanum, didymium, and erbium) as well as from the alkaline earths.

12. **Potassium Sulfate** added to a concentrated solution of an aluminium salt causes the formation of potash alum, $KAl(SO_4)_2 \cdot 12\,H_2O$. Crystals of similar alums can be formed with other elements of the alkali group, particularly rubidium and cesium. The last-mentioned element forms a difficultly soluble alum.

13. **Tincture of Alkanna** added to a neutral solution of an aluminium salt gives a reddish-violet color with orange-yellow fluorescence. In a dilute solution, characteristic absorption bands are obtained in spectrum analysis.§

Detection of Aluminium in the Presence of Organic Substances which Prevent the Precipitation by the Above Reagents

The presence of tartaric acid or other non-volatile, organic hydroxy-compound prevents the precipitation with above reagents.* To detect the presence of aluminium

* *Z. anal. Chem.*, **31**, 222.
† *Ibid.*, 3, 362.
‡ *Chem. Zentr.*, **1916**, I, 176.
§ Formánek, *Z. anal. Chem.*, **39**, 416.

in such cases, the organic substance must be destroyed. This is best accomplished as follows: Add some sodium carbonate and a little potassium nitrate to the solution, evaporate to dryness in a platinum dish, and ignite the residue, whereby the aluminium becomes aluminate and the organic substance is destroyed with separation of carbon. Treat the residue with dilute nitric acid and filter; the aluminium goes into solution as nitrate and can be precipitated with any of the above reagents.

If sufficient nitrate was present, the carbon will be completely burnt to CO_2, and the residue then often contains undecomposed nitrate or nitrite. It would, therefore, be unwise to treat the residue in the platinum dish with hydrochloric acid, as aqua regia would be formed and the platinum would be dissolved. Consequently the residue is treated with nitric acid (or with hydrochloric acid in a porcelain dish).

When strongly ignited, aluminium hydroxide loses water and forms the anhydride, Al_2O_3, which is scarcely soluble at all in hydrochloric and nitric acids. In hot, concentrated sulfuric acid, with a little water, it will dissolve after long digestion. Ignited aluminium oxide, as well as the mineral corundum, is most readily brought into solution by fusion with potassium pyrosulfate. The fusion is accomplished in the following way: Take twelve times as much fused potassium acid sulfate as there is oxide to get into solution and heat it by itself in a large platinum crucible over a small flame. The acid potassium sulfate melts readily, at about 300° C., gives off water (causing frothing), and becomes changed into potassium pyrosulfate:

$$2\,KHSO_4 \rightarrow H_2O + K_2S_2O_7.$$

As soon as the frothing has ceased, the transformation into potassium pyrosulfate is complete. Add the dry aluminium oxide to the crucible and continue heating until the melt begins to solidify (showing that a considerable amount of potassium sulfate, which melts much more difficultly than the pyrosulfate, has been formed), then raise the temperature and continue heating until the oxide has dissolved clear in the melt. By heating the pyrosulfate, SO_3 is given off, which at the high temperature is very active:

$$K_2S_2O_7 = K_2SO_4 + SO_3.$$

If the heating is too rapid, much of the SO_3 is lost.

After the reaction is complete, the melt contains the aluminium as aluminium sulfate in the presence of potassium sulfate,

$$3\,K_2S_2O_7 + Al_2O_3 = Al_2(SO_4)_3 + 3\,K_2SO_4,$$

and both of these substances can be dissolved by water.

The ignited aluminium oxide can also be brought into solution by fusion with caustic alkalies:

$$Al_2O_3 + 2\,KOH = 2\,KAlO_2 + H_2O.$$

This last operation is usually carried on in a silver crucible, never in platinum, as the latter would be strongly attacked.

Native Al_2O_3 (corundum, ruby, sapphire, emery) can be completely brought into solution by fusion with potassium pyrosulfate.

Reactions in the Dry Way

Aluminium compounds, on being heated with sodium carbonate on charcoal before the blowpipe give a white, infusible, brightly glowing oxide, which, when moistened with cobalt nitrate solution and again heated, becomes a blue infusible mass (Thénard's blue):

$$Al_2O_3 + CoO = CoAl_2O_4.$$

In carrying out this test it is extremely important not to use an excess of cobalt nitrate, for this salt leaves black cobalt oxide behind on ignition and when an excess is present it entirely obscures the blue color of cobaltous aluminate.

The test is usually applied to a precipitate of aluminium hydroxide. A good way to carry out the test is as follows: Dissolve the precipitate in 5 cc. of 6 N nitric acid and add to the solution half as many small drops of 1 per cent cobalt nitrate solution as there are presumable milligrams of aluminium present. Evaporate the solution nearly to dryness, add a few drops of water and moisten a roll of filter paper with the concentrated solution. Heat over the flame until the paper is entirely consumed and then very strongly.

Thénard's blue is infusible. If a fused mass is obtained in this test, the presence of aluminium is doubtful, because all fused glasses, such as borax beads, sodium phosphate beads, etc., are colored blue by cobalt oxide. The blue color is also obtained with certain other infusible compounds containing no aluminium, e.g., alkaline earth phosphates.

Aluminium salts are not volatile, and do not color the flame. By ignition in the air, all aluminium salts, with the exception of the phosphate and silicate, are decomposed, leaving behind the oxide:

$$4\,AlCl_3 + 3\,O_2 = 2\,Al_2O_3 + 6\,Cl_2,$$

$$2\,Al(NO_3)_3 = Al_2O_3 + 3\,N_2O_5,$$

$$Al_2(SO_4)_3 = Al_2O_3 + 3\,SO_3.$$

CHROMIUM, Cr. At. Wt. 52.0

Sp. Gr. = 6.81. M. Pt. = 1510° C.

Occurrence. — Chromium occurs in nature as chromite, $FeCr_2O_4$, isomorphous with spinel (see aluminium); as monoclinic crocoite, $PbCrO_4$; and as laxmannite, a double compound of lead-copper phos-

phate and basic lead chromate, $(Pb,Cu)_3(PO_4)_2 \cdot Pb_2O(CrO_4)_2$. *Furthermore, it is found in small quantities in many silicates, such as muscovites, biotites, augites, etc., and consequently in their weathering products, as in many kaolins, bauxite, etc.*

Metallic chromium is white, crystalline and brittle; it is easily reduced to powder. The metal dissolves in hydrochloric, hydrobromic, hydriodic, sulfuric and oxalic acids with evolution of hydrogen and formation of chromous, or a mixture of chromous and chromic, salts. The metal is easily made passive, however, by immersion in nitric acid or by anodic polarization. Passive chromium retains its luster in the air, is insoluble in dilute acids and resembles the noble metals. With oxygen chromium forms the following oxides: chromous oxide, CrO; chromic oxide, Cr_2O_3; chromic acid anhydride, CrO_3; and chromium peroxides corresponding to CrO_4, Cr_2O_9, Cr_2O_{11} and Cr_2O_{13} (cf. p. 147).

The oxides CrO and Cr_2O_3 are basic anhydrides, and, on being dissolved in acids, yield the corresponding salts, the chromous and the chromic compounds. Chromium trioxide is the anhydride of the hypothetical chromic acid, H_2CrO_4 and forms chromates with bases. The chromium peroxides have never been obtained pure; salts of perchromic acid have been isolated and analyzed. (Cf. p. 147.)

I. Chromous Compounds

Chromous oxide is known only in the form of its hydroxide, $Cr(OH)_2$, which, on being dried, loses hydrogen and water, leaving behind chromic oxide:

$$2\,Cr(OH)_2 = H_2 + H_2O + Cr_2O_3.$$

Like chromous hydroxide, all chromous compounds are extremely unstable, being changed readily by contact with the air into chromic compounds. Only the *halogen* compounds, the *phosphate, carbonate,* and *acetate,* are known in the dry state; the sulfate only in solution. The acetate, $Cr(C_2H_3O_2)_2 + H_2O$, is a reddish-brown, crystalline substance, insoluble in water, but readily soluble in hydrochloric acid. This solution, as well as that of all chromous salts, absorbs oxygen with avidity, and is consequently used in gas analysis for the determination of oxygen in gas mixtures. Solutions of chromous compounds are obtained by the reduction of chromic compounds with zinc and acid out of contact with the air.

On account of the instability of these compounds the analytical chemist will rarely meet them and further description is unnecessary.

II. Chromic Compounds

All chromic compounds contain chromium as a trivalent element; they are colored either green or violet, and are soluble in water as a rule. The *oxide, hydroxide, phosphate, anhydrous chloride,* and the *sulfate,* after being strongly heated in a stream of carbon dioxide gas, are insoluble in water. Violet chromium chloride, obtained in the dry way, is insoluble in acids; it dissolves readily in water containing a trace of chromous chloride, or in the presence of stannous chloride (tin and hydrochloric acid). By dissolving the grayish-green chromic hydroxide in acids, green solutions are always obtained, which on long standing become greenish violet or violet, but on boiling become green again. Chromic sulfate forms with sulfates of potassium, ammonium, cesium, or rubidium, the so-called chrome-alums, which crystallize in the regular system. These alums, like all other chromic salts, react acid in aqueous solution (hydrolysis).

Crystals are obtained by evaporation of the violet solutions; the green solutions either give uncrystallizable sirups or are changed into violet crystals. The addition of nitric acid favors the change of the green into the violet modification. Probably the green modification corresponds to a more or less basic salt and the violet modification to the violet salt.* Often the green salt contains a complex ion. Chromium shows a great tendency to form complex ions with hydrocyanic and sulfuric acids, organic compounds containing hydroxyl, and with ammonia, amines, pyridine, etc. These complex compounds do not show many of the characteristic chromium reactions.

Chromic sulfide, Cr_2S_3, can be obtained only in the dry way. On being treated with water it is decomposed quantitatively into hydroxide and hydrogen sulfide.

Reactions in the Wet Way

1. **Ammonia** produces a grayish-green, gelatinous precipitate of chromic hydroxide:

$$Cr^{+++} + 3\,OH^- \rightarrow Cr(OH)_3.$$

Chromic hydroxide is somewhat soluble in excess of ammonia, forming a violet or pink solution, particularly soluble when the ammonia is added to a *violet* solution of a chromic salt, in the presence of ammonium salts. This is caused by the formation of complex chromic-ammonia cations, which, however, may be decomposed by boiling the solution until the excess of ammonia has been driven off, when the chromium is quantitatively precipitated as hydroxide. In order, then,

* Recoura, *Bull. soc. Chim.* [3], **6**, 909; Whitney, *Z. phys. Chem.*, **20**, 40.

to precipitate the chromium from a solution as hydroxide, it is necessary to precipitate at a boiling temperature, and to use as little ammonia as possible.

By ignition of chromic hydroxide, green chromic oxide is obtained, which after strong ignition is insoluble in acids. In order to bring it into solution, it must be fused with potassium pyrosulfate (cf. aluminium, p. 138); or with an oxidizing flux such as sodium carbonate and potassium nitrate in a platinum crucible or sodium peroxide in a nickel or iron crucible, whereby sodium chromate is formed:

$$2\,Cr_2O_3 + 4\,Na_2CO_3 + 3\,O_2 = 4\,Na_2CrO_4 + 4\,CO_2\uparrow.$$

If the product of this last fusion is dissolved in water, acidified with hydrochloric acid, and boiled with alcohol, a green solution of chromic chloride will be obtained (p. 146), from which the chromium can be precipitated as hydroxide with ammonia. On fusing with sodium carbonate and potassium nitrate in a platinum crucible, the crucible will always be slightly attacked, so that a small amount of platinum will go into solution with the fused mass; it can be removed, after the treatment with hydrochloric acid, by passing hydrogen sulfide into the boiling solution, and filtering off the precipitated platinum sulfide.

2. **Potassium** and **Sodium Hydroxides** cause the same precipitation as ammonia; but the precipitate is readily soluble in excess of the reagent, forming a green chromite:

$$Cr^{+++} + 3\,OH^- \rightarrow \mathbf{Cr(OH)_3};\ \mathbf{Cr(OH)_3} + OH^- \rightleftarrows CrO_2^- + 2\,H_2O.$$

Chromic hydroxide behaves here as a weak acid. The reaction is reversible, the presence of considerable water causing the reaction to go from right to left, particularly at the boiling temperature. By boiling the dilute solution, complete hydrolysis takes place; the chromium is almost quantitatively precipitated as hydroxide (differing from aluminium).

Chromic hydroxide often causes the precipitation of other bases as insoluble chromites, particularly zinc and magnesium.

3. **Sodium Peroxide** and caustic alkali added to the solution of a chromic salt convert the trivalent chromium into the chromate ion in which the chromium has a positive valence of six:

$$2\,Cr^{+++} + 3\,Na_2O_2 + 4\,OH^- \rightarrow 2\,CrO_4^{--} + 6\,Na^+ + 2\,H_2O.$$

4. **Alkali Carbonates, Barium Carbonate, Ammonium Sulfide,** and **Alkali Thiosulfates** precipitate chromic hydroxide, as with aluminium.

5. **Alkali Phosphates** give a greenish, amorphous precipitate of chromic phosphate:

$$2\,HPO_4^{--} + Cr^{+++} \rightarrow CrPO_4 + H_2PO_4^-.$$

Chromic phosphate is readily soluble in mineral acids and in cold acetic acid. On boiling the acetic acid solution, chromic phosphate

separates out again. Oxalic acid prevents the precipitation of chromic phosphate owing to the formation of a complex chrome-oxalate ion.

The precipitation of chromic hydroxide, by any of the reactions here described, is also prevented by tartaric, citric and oxalic acids and by sugar. Sometimes no precipitation at all is obtained and in all cases the precipitation is incomplete.

6. **Alkali Acetates** produce in solutions of chromic salts no precipitation, even when the solutions are boiled. If, however, considerable amounts of aluminium and ferric salts are present at the same time, the chromium will be precipitated almost quantitatively with the iron and aluminium as basic acetate. In case, however, chromium predominates, only a part of the metals will be precipitated as basic salts; the filtrate will contain iron and aluminium with chromium. *In the presence of chromium, the basic acetate separation is always uncertain.*

7. **Hydrogen Sulfide** produces no precipitate in acid solutions of chromic salts.

III. Chromates

Chromium trioxide, CrO_3, forms red orthorhombic needles, which dissolve readily in water to an orange-red solution. If this solution is neutralized with potassium hydroxide, it becomes yellow, and on evaporation yellow K_2CrO_4, the potassium salt of chromic acid, H_2CrO_4, is obtained. If the yellow solution of potassium chromate is acidified, and then allowed to crystallize, orange-red prisms of triclinic potassium dichromate crystals, $K_2Cr_2O_7$, are formed.

The aqueous solution of potassium chromate, K_2CrO_4, contains colorless potassium ions and yellow CrO_4^{--} anions, while the aqueous solution of potassium dichromate, $K_2Cr_2O_7$, contains, in the presence of the colorless potassium ions, the orange-red colored $Cr_2O_7^{--}$ anions:

$$K_2Cr_2O_7 \rightleftarrows 2\,K^+ + Cr_2O_7^{--}.$$

We are able, therefore, to determine from the color of a chromate solution the nature of the chromate ion which is present.

The free acids, H_2CrO_4 and $H_2Cr_2O_7$, cannot be isolated, but only the corresponding anhydride, CrO_3, which is very soluble in water. When chromium trioxide dissolves in water, the following reaction takes place:

$$CrO_3 + H_2O \rightleftarrows H_2CrO_4.$$

The first hydrogen of this acid belongs to the class of very strong acids (cf. p. 10) and consequently the greater part of the H_2CrO_4 undergoes ionization as fast as it is formed: $H_2CrO_4 \rightleftarrows H^+ + HCrO_4^-$. The second hydrogen, on the other hand, corresponds to that of a very weak acid and we may say that in the presence of hydrogen ions $HCrO_4^-$ is scarcely ionized at all. The $HCrO_4^-$, however, enters into the following equilibrium: $2\,HCrO_4^- \rightleftarrows H_2O + Cr_2O_7^{--}$. The presence of hydrogen ions

will evidently favor the formation of the dichromate ion, while dilution will favor the reverse reaction, and the presence of OH^- ions will cause the dichromate ions to disappear and yellow CrO_4^{--} ions will take their place.

Remark. — Although we may judge as to the color of the ions from the color of the solution, and often predict what the color of the solid salt will be, yet, on the other hand, we cannot tell what the color of the solution will be from that of the salt itself. Yellow lead iodide dissolves in water to a colorless solution, and the yellow and red iodides of mercury, although only slightly soluble, also do not yield colored solutions.

If the solution of a salt is colored, the salt itself will be colored; but the reverse is not always true.

All chromates are insoluble in water, except those of the alkalies, calcium, strontium and magnesium. All chromates dissolve in nitric acid, except fused lead chromate, which dissolves with difficulty.

Formation of Chromates

All chromium compounds may be readily oxidized to chromates. According to whether the compound is soluble in water or not, different methods are used to effect the oxidation.

The student should not attempt to memorize a large number of chemical equations, but he should strive to become able to express his chemical knowledge in the form of equations or equilibria expressions. To balance equations representing the oxidation of chromium, it should be remembered that the chromium is changed from a positive valence of three (in the form of chromic cations or chromite anions) to a positive valence of six (in the form of chromic acid, chromate or dichromate ions). When the oxidation takes place by means of halogen, a halide is formed and the halogen is changed from the neutral condition to the form of a negative ion with unit charge. When hypochlorite is the oxidizing agent, the unit positive charge on the chlorine atom is lost and a unit negative charge takes its place, which corresponds to the loss of two positive charges. Similarly, lead peroxide and hydrogen peroxide have an oxidizing power corresponding to the loss of two unit charges of positive electricity.

The valence of the chromium in the anions CrO_2^-, CrO_4^{--} and $Cr_2O_7^{--}$ is found, in accordance with the rule given on p. 25, by subtracting the charge of the ion from the product obtained by multiplying the number of oxygen atoms present in the ion by its valence of two. In equilibrium expressions it is important to make sure that the algebraic sum of the positive and negative charges on one side is exactly the same as the algebraic sum of the charges on the other. With a little practice it is very easy to determine whether hydrogen ions, hydroxyl ions or water molecules are required to make the equation balance.

The oxidation in alkaline solutions is effected:

(*a*) By the halogens. If sodium or potassium hydroxide is added in excess to a solution of a chromic salt, and chlorine or bromine is conducted into the solution, the oxidation will be complete in a few minutes: the green chromite becomes yellow chromate:

$$2\,CrO_2^- + 8\,OH^- + 3\,Cl_2 \rightarrow 2\,CrO_4^{--} + 6\,Cl^- + 4\,H_2O.$$

Chromic compounds may also be oxidized by halogens in the presence of sodium acetate, the reaction going extremely slowly in the cold, but very quickly on warming:

$$2\,Cr^{+++} + 3\,Cl_2 + 8\,H_2O \rightleftarrows 2\,CrO_4^{--} + 6\,Cl^- + 16\,H^+.$$

The sodium acetate greatly lowers the concentration of the hydrogen ions and causes the reaction to proceed slowly from left to right (cf. p. 47).

(*b*) By hypochlorites (sodium hypochlorite, chloride of lime, etc.):

$$2\,CrO_2^- + 3\,OCl^- + 2\,OH^- \rightarrow 2\,CrO_4^{--} + 3\,Cl^- + H_2O.$$

(*c*) By lead peroxide. The alkaline solution is boiled with lead peroxide:

$$2\,CrO_2^- + 3\,PbO_2 + 8\,OH^- \rightarrow 3\,PbO_2^{--} + 2\,CrO_4^{--} + 4\,H_2O.$$

(*d*) By hydrogen peroxide,

$$2\,CrO_2^- + 3\,H_2O_2 + 2\,OH^- \rightarrow 2\,CrO_4^{--} + 4\,H_2O,$$

the reaction taking place on warming.

(*e*) By freshly-precipitated manganese dioxide. The oxidation takes place on boiling the neutral or slightly acid solution:

$$2\,Cr^{+++} + 3\,MnO_2 + 4\,OH^- \rightarrow 2\,CrO_4^{--} + 3\,Mn^{++} + 2\,H_2O.$$

It is evident from this last equilibrium expression that the presence of hydroxyl ions should favor the oxidation and hydrogen ions should hinder it. On the other hand, manganese dioxide is very insoluble in alkaline solutions. It is necessary, therefore, to have the solution neutral or slightly acid in order to obtain a sufficient concentration of quadrivalent manganese in solution.

In acid solutions the chromic cation is the most stable condition for chromium, but in alkaline solutions the chromate anion is the more stable condition. In acid solutions, therefore, it is easy to reduce a chromate to chromic salt and in alkaline solutions it is easy to oxidize a chromic salt to chromate.

Oxidation in acid solution may be effected by boiling with very energetic oxidizing agents such as concentrated nitric acid and potassium chlorate, sodium bismuthate (or bismuth tetroxide), or potassium permanganate:

$$2\,Cr^{+++} + 3\,NaBiO_3 + 4\,H^+ \rightarrow Cr_2O_7^{--} + 3\,Na^+ + 3\,Bi^{+++} + 2\,H_2O.$$

In carrying out this reaction the chloride should not be used, or any other salt of which the anion is capable of oxidation; the acid used should be nitric or sulfuric acid.

In the case of an insoluble chromium compound, such as strongly ignited chromic oxide, or the mineral chromite, the oxidation is effected by means of fusion with sodium carbonate and an oxidizing agent such as potassium nitrate, potassium chlorate or sodium peroxide (cf. pp.

142, 149). The alkali chromates thus obtained are of a deep-yellow color, and are readily soluble in water.

Reduction of Chromates

Chromic acid, chromates and dichromates are strong oxidizing agents in acid solutions. The oxidations take place even in very dilute solution, and for this reason potassium dichromate is often used in quantitative analysis, the quantity of reducing agent being determined by the volume of potassium dichromate required to react with it. Ferrous ions, sulfurous acid, hydrogen sulfide and hydriodic acid are oxidized at the ordinary temperature. Oxalic acid and alcohol are oxidized slowly at the laboratory temperature and very quickly on heating the solution; hydrochloric acid and hydrobromic acid only when the solution is hot. The original orange solution is changed to green, the color of chromic ions:

$$Cr_2O_7^{--} + 6\,Fe^{++} + 14\,H^+ \rightarrow 2\,Cr^{+++} + 6\,Fe^{+++} + 7\,H_2O,$$

$$Cr_2O_7^{--} + 3\,SO_3^{--} + 8\,H^+ \rightarrow 2\,Cr^{+++} + 3\,SO_4^{--} + 4\,H_2O,$$

$$Cr_2O_7^{--} + 3\,H_2S + 8\,H^+ \rightarrow 2\,Cr^{+++} + 3\,S + 7\,H_2O,$$

$$Cr_2O_7^{--} + 3\,H_2C_2O_4, + 8\,H^+ \rightarrow 2\,Cr^{+++} + 6\,CO_2 + 7\,H_2O,$$

$$Cr_2O_7^{--} + 6\,I^- + 14\,H^+ \rightarrow 2\,Cr^{+++} + 3\,I_2 + 7\,H_2O,$$

$$Cr_2O_7^{--} + 6\,HCl + 8\,H^+ \rightarrow 2\,Cr^{+++} + 3\,Cl_2\uparrow + 7\,H_2O.$$

As this last reaction takes place only on warming, it furnishes us with a convenient method for preparing small quantities of chlorine for analytical purposes, because the evolution of chlorine ceases as soon as the lamp is taken away. It is necessary, however, to employ an excess of hydrochloric acid, as otherwise no chlorine will be evolved owing to the formation of potassium chlorochromate, $KCrO_3Cl$:

$$Cr_2O_7^{--} + 2\,HCl \rightarrow 2\,CrO_3Cl^- + H_2O,$$

which is decomposed on adding more hydrochloric acid:

$$2\,CrO_3Cl^- + 4\,HCl + 8\,H^+ \rightarrow 2\,Cr^{+++} + 6\,H_2O + 3\,Cl_2\uparrow.$$

If alcohol and hydrochloric acid are allowed to act simultaneously upon a chromate (the reaction takes place on gentle warming without the evolution of chlorine), the alcohol is oxidized to aldehyde:

$$Cr_2O_7^{--} + 3\,C_2H_5OH + 8\,H^+ \rightarrow 2\,Cr^{+++} + 7\,H_2O + 3\,\underset{\text{Aldehyde}}{CH_3CHO}.$$

This last reaction is often used for reducing a chromate, because the aldehyde (recognizable by its peculiar empyreumatic odor) and the excess of alcohol are easily removed by boiling the solution, and the latter then contains simply the chromium and the metal of the chromate as chlorides.

By boiling chromates with concentrated sulfuric acid, reduction takes place with evolution of oxygen:

$$2\,K_2Cr_2O_7 + 8\,H_2SO_4 = 2\,K_2SO_4 + 2\,Cr_2(SO_4)_3 + 8\,H_2O + 3\,O_2\uparrow.$$

The behavior of *free chromic acid* toward *hydrogen peroxide* is characteristic. The chromic acid is converted into blue perchromic acids which are soluble in ether: H_7CrO_{10}, H_3CrO_7 or H_3CrO_8.

If a *cold, alkaline* solution of a chromate is treated with neutral hydrogen peroxide, the solution is colored red, owing to the formation of an alkali salt of perchromic acid, H_3CrO_8:

$$2\,K_2CrO_4 + 7\,H_2O_2 + 2\,KOH = 8\,H_2O + 2\,K_3CrO_8.$$

Little by little the red color disappears, with evolution of oxygen, and the yellow color of the chromate returns:

$$4\,K_3CrO_8 + 2\,H_2O = 4\,KOH + 4\,K_2CrO_4 + 7\,O_2\uparrow.$$

If a *cold, neutral* solution of potassium dichromate is treated with hydrogen peroxide, the solution is colored violet, due to the formation of the potassium salt of a slightly different perchromic acid, H_3CrO_7:

$$K_2Cr_2O_7 + 5\,H_2O_2 = 3\,H_2O + 2\,KH_2CrO_7.$$

In this case, also, the violet color gradually disappears with evolution of oxygen and regeneration of the dichromate:

$$4\,KH_2CrO_7 = 2\,K_2Cr_2O_7 + 5\,O_2\uparrow + 4\,H_2O.$$

If either the red or violet solution, obtained as above described, is shaken with ether, the latter remains colorless.

The behavior of chromate solutions toward an excess of hydrogen peroxide in the presence of dilute sulfuric acid is quite different. There is then formed invariably the perchromic acid richest in oxygen, H_7CrO_{10}, and the solution is turned an intense blue. The blue color disappears after a short time and the solution turns green, owing to the conversion of all the chromium into the chromic condition:

$$2\,H_7CrO_{10} + 3\,H_2SO_4 = Cr_2(SO_4)_3 + 10\,H_2O + 5\,O_2\uparrow.$$

This perchromic acid is very soluble in ether; if, therefore, the aqueous solution is shaken with ether the latter becomes colored a beautiful blue. In fact, this acid is more stable in ethereal than in aqueous solution.

Since the formation of the intense-blue-colored perchromic acid takes place so readily, it may be used as a basis for a sensitive test for free chromic acid, which is made as follows: Add a few drops of dilute sulfuric acid to one or two cubic centimeters of hydrogen peroxide and shake with 2 cc. of ether; then add a little of the chromate solution and shake the mixture again. In the presence of 0.1 mg. of

chromic acid, the upper ether layer is colored intensely blue, and the reaction is noticeable with only 0.007 mg. of chromic acid (Lehner).

Most chromates are insoluble in water, and exhibit characteristic colors; therefore it is easiest to test for chromium when it is present as a chromate. The test for oxidizing constituents with $MnCl_2$ in concentrated hydrochloric acid (cf. p. 491) is easily obtained with a chromate.

Reactions for the Precipitation of Chromic Acid

1. **Sulfuric Acid.** — *Dilute* sulfuric acid causes, at the most, a change of color from yellow to orange, without any evolution of gas.

Concentrated sulfuric acid causes the cold solution to change to orange color, and there is often a separation of red needles of CrO_3; the solution on being heated becomes green, the chromic acid being reduced to chromic salt with evolution of oxygen:

$$4\,CrO_3 + 6\,H_2SO_4 = 6\,H_2O + 3\,O_2\uparrow + 2\,Cr_2(SO_4)_3.$$

2. **Silver Nitrate** produces in neutral chromate solutions a brownish-red precipitate of silver chromate:

$$CrO_4^{--} + 2\,Ag^+ \rightarrow \mathbf{Ag_2CrO_4},$$

soluble in ammonia and mineral acids (hydrochloric acid changes it into insoluble silver chloride and chromic acid), insoluble in acetic acid. If to a moderately concentrated solution of potassium dichromate, silver nitrate be added, a reddish-brown precipitate of silver dichromate is formed:

$$Cr_2O_7^{--} + 2\,Ag^+ \rightarrow \mathbf{Ag_2Cr_2O_7},$$

which, on being boiled with water, is changed into the less soluble normal silver chromate:

$$\mathbf{2\,Ag_2Cr_2O_7} + H_2O \rightarrow \mathbf{2\,Ag_2CrO_4} + H_2Cr_2O_7.$$

The presence of sodium acetate causes this change to take place in the cold (cf. pp. 47 and 143).

3. **Lead Acetate** produces in solutions of normal chromates and dichromates a yellow precipitate of lead chromate, which is soluble in nitric acid but insoluble in acetic acid:

$$CrO_4^{--} + Pb^{++} \rightarrow \mathbf{PbCrO_4},$$

$$Cr_2O_7^{--} + 2\,Pb(C_2H_3O_2)_2 + H_2O \rightarrow 2\,HC_2H_3O_2 + 2\,C_2H_3O_2^- + \mathbf{2\,PbCrO_4}.$$

If lead nitrate is used instead of lead acetate, the precipitation is not complete unless sodium acetate is added.

4. **Barium Chloride** produces in solutions of normal chromates a yellow precipitate of barium chromate:

$$CrO_4^{--} + Ba^{++} \rightarrow \mathbf{BaCrO_4},$$

soluble in mineral acids, insoluble in acetic acid. From solutions of dichromates the precipitation is complete only on addition of an alkali acetate (cf. p. 115).

5. **Mercurous Nitrate** produces in the cold a brown, amorphous precipitate of mercurous chromate:

$$CrO_4^{--} + Hg_2(NO_3)_2 \rightarrow \mathbf{Hg_2CrO_4} + 2\,NO_3^-,$$

which on being boiled becomes fiery-red and crystalline.

Behavior of Chromium Trioxide and Chromates on Ignition

Chromium trioxide is decomposed on ignition into chromic oxide and oxygen, $4\,CrO_3 = 2\,Cr_2O_3 + 3\,O_2\uparrow$. The chromates of ammonium and mercury behave quite similarly. Thus *normal ammonium chromate* on ignition is changed to *chromic oxide, ammonia, nitrogen,* and *water.* The reduction of the chromate is favored by the reducing action of ammonia which is present in excess.

$$2\,(NH_4)_2CrO_4 = 2\,NH_3\uparrow + N_2\uparrow + 5\,H_2O\uparrow + Cr_2O_3.$$

Ammonium Dichromate evolves only water and nitrogen:

$$(NH_4)_2Cr_2O_7 = 4\,H_2O\uparrow + N_2\uparrow + Cr_2O_3.$$

This decomposition takes place violently with scintillation. The chromic oxide which remains behind is very voluminous and reminds one of tea-leaves; consequently it is sometimes called "tea-leaved chromic oxide."

Mercurous Chromate is decomposed on ignition into *chromic oxide, mercury vapors,* and *oxygen:*

$$4\,Hg_2CrO_4 = 2\,Cr_2O_3 + 8\,Hg\uparrow + 5\,O_2\uparrow.$$

The Dichromates of the Alkalies are changed on ignition into normal chromates, chromic oxide, and oxygen:

$$4\,K_2Cr_2O_7 = 4\,K_2CrO_4 + 2\,Cr_2O_3 + 3\,O_2\uparrow.$$

Reactions of Chromium in the Dry Way

All chromium compounds color the borax, or salt of phosphorus, bead an emerald green both in the oxidizing and reducing flames. Heated with sodium carbonate on charcoal before the blowpipe, all chromium compounds yield a green slag, which after long heating is changed to green infusible chromic oxide. By fusing with sodium carbonate and potassium nitrate in the loop of a platinum wire, all chromium compounds yield a yellow melt of alkali chromate:

$$2\,Cr_2O_3 + 4\,Na_2CO_3 + 3\,O_2 = 4\,Na_2CrO_4 + 4\,CO_2\uparrow.$$

If the fused mass is dissolved in water and acidified with acetic acid, the solution will give with silver nitrate a reddish-brown precipitate of silver chromate. This reaction is very delicate and serves for the detection of minute traces of chromium. Cloth which has been dyed with a chromium mordant can be tested in this way; the ash from a thread 5 cm. long is sufficient to give the test.

IRON, Fe. At. Wt. 55.84

Sp. Gr. 7.98. M. Pt. about 1600° C.

Occurrence. — Native iron is rarely found. It occurs in basaltic rocks; also in meteorites, associated with nickel, cobalt, carbon, sulfur, and phosphorus.

The most important iron ores are the oxides and sulfides. Of these may be mentioned:

Hematite, Fe_2O_3, isomorphous with corundum; magnetite, Fe_3O_4, isomorphous with spinel; goethite, $FeHO_2$, isomorphous with diaspore and manganite; limonite, $Fe_4H_6O_9$; (bog ore), $Fe(OH)_3$, which is used in the purification of illuminating gas; pyrite, FeS_2, which crystallizes in the isometric system; marcasite, FeS_2, orthorhombic. Iron disulfide is, therefore, dimorphous. Another important iron ore is siderite, $FeCO_3$, which is rhombohedral; vivianite, $Fe_3(PO_4)_2 \cdot 8\ H_2O$, is monoclinic.

The metallic iron of commerce is rarely pure, but usually contains more or less *iron carbide, iron sulfide, iron phosphide, iron silicide,* corresponding *manganese* compounds *graphite,* etc.

On dissolving commercial iron in acids (H_2SO_4,HCl), hydrogen, and small amounts of hydrocarbons, hydrogen sulfide, mercaptans, phosphuretted hydrogen, and silicon hydride are evolved, and these impurities give to the gas its unpleasant odor. There remains almost always an undissolved residue consisting chiefly of carbon.

The result of the action of nitric acid upon metallic iron depends upon the concentration of the acid and the temperature. With dilute nitric acid the reaction may take place without evolution of gas and the formation of ferrous and ammonium ions:

$$4\,Fe + 10\,H^+ + NO_3^- \rightarrow 4\,Fe^{++} + NH_4^+ + 3\,H_2O.$$

When the nitric acid is more concentrated, ferric ions are formed and nitrous oxide, or, with strong acid, nitrogen peroxide is evolved:

$$Fe + 4\,HNO_3 \rightarrow Fe(NO_3)_3 + 2\,H_2O + NO\uparrow$$
$$Fe + 6\,HNO_3 \rightarrow Fe(NO_3)_3 + 3\,H_2O + 3\,NO_2\uparrow.$$

Cold, concentrated nitric acid makes iron passive; in this condition

it does not react with cold, dilute nitric acid or deposit copper from the aqueous solution of a cupric salt.

Iron is bivalent, trivalent, and rarely hexavalent, forming the following oxides:

Iron protoxide or ferrous oxide	Iron sesquioxide or ferric oxide	Ferrous-ferric oxide or magnetite	Iron trioxide
FeO	Fe_2O_3	Fe_3O_4	(FeO_3).

Iron trioxide, FeO_3, containing hexavalent iron, has never been isolated. It plays the part of an acid anhydride in ferrates of the general formula R_2FeO_4, which are decomposable by water.

By dissolving the three known oxides in acid the corresponding salts are obtained: thus ferrous oxide gives with hydrochloric acid, ferrous chloride,

$$FeO + 2\,HCl = H_2O + FeCl_2;$$

ferric oxide gives ferric chloride,

$$Fe_2O_3 + 6\,HCl = 3\,H_2O + 2\,FeCl_3,$$

while ferrous-ferric oxide yields a mixture of ferrous and ferric chlorides:

$$Fe_3O_4 + 8\,HCl = 4\,H_2O + 2\,FeCl_3 + FeCl_2.$$

Iron, therefore, forms two series of salts: first, the ferrous, derived from ferrous oxide, containing bivalent iron; second, the ferric, derived from ferric oxide, containing trivalent iron. These two series of salts show a quite different behavior toward reagents.

The salts of bivalent iron (ferrous salts) are white when anhydrous but are greenish with water of crystallization; the solutions are colorless when dilute and greenish when concentrated. Ferrous salts are oxidized somewhat by exposure to the air and in solution they are oxidized by dissolved oxygen; this results in the formation of a basic salt, e.g.:

$$4\,FeSO_4 + O_2 \rightarrow 2\,Fe_2O(SO_4)_2$$

or,

$$4\,FeSO_4 + O_2 + 2\,H_2O \rightarrow 4\,Fe\begin{matrix}\diagup OH \\ \diagdown SO_4.\end{matrix}$$

The position of iron in the electromotive series shows that it is capable of being oxidized by hydrogen ions and suggests the possibility of its being oxidized to a measurable extent by the hydrogen ions of water. Careful experiments have shown that absolutely pure water containing no dissolved oxygen, does not affect iron appreciably at ordinary laboratory temperatures, though there is evidence that a trace of iron dissolves and a film of hydrogen is formed on the metal which acts as a check upon further attack. The position of ferrous iron in the voltage series shows that hydrogen ions cannot oxidize iron appreciably to the ferric condition. The presence of dissolved oxygen, and this is normally present in all water that is exposed to the atmosphere, can accomplish this oxidation of the ferrous ions to the ferric condition and it also aids in the oxidation of the iron from the metallic

to the ferrous state. In this way iron exposed to moisture and oxygen oxidizes or *rusts*. The rusting process is favored by the contact of the metal with a more noble metal, such as platinum, copper or nickel; an electric couple is formed and the iron becomes the positive pole, so that the hydrogen set free by the action of iron upon water is deposited upon the more noble metal. The presence of a less noble metal, such as zinc, tends to hinder the corrosion of iron; the zinc corrodes instead of the iron.

The presence of an acid is, therefore, not absolutely necessary to start the corrosion of iron. An increase in the concentration of hydrogen ions, however, will greatly hasten the solution of the metal. When carbonic acid is present, ferrous bicarbonate is first formed and, when the ferrous iron is oxidized to the ferric condition, the carbonic acid is set free again because ferric carbonate does not exist. The acid again acts upon the metal and the rate of its corrosion is greatly accelerated.

Certain substances tend to make iron *passive*, particularly strong nitric acid. Passive iron does not dissolve in dilute nitric acid and does not corrode readily (cf. aluminium, p. 133). On the other hand, certain substances can overcome the passive condition and are said to *activate* the iron. Thus a solution of common salt is an activating agent.

Different varieties of iron and steel corrode with different degrees of readiness. Cast iron is often protected by its *casting skin*. Impurities present in steel often favor corrosion by causing electric couples to be established.

A. Ferrous Compounds

Ferrous compounds, which may be prepared by dissolving metallic iron, ferrous oxide, ferrous hydroxide, ferrous carbonate, or ferrous sulfide, etc., in acids, are usually greenish in the crystallized state, but in the anhydrous condition they are white, yellow or bluish; in concentrated solution they are green; in dilute solutions almost colorless. Ferrous compounds exhibit a strong tendency to change over into ferric salts; they are strong reducing agents.

Reactions in the Wet Way

1. **Ammonia** produces in neutral solutions an incomplete precipitation of white ferrous hydroxide:

$$FeCl_2 + 2\,NH_3 + 2\,H_2O \rightleftarrows \mathbf{Fe(OH)_2} + 2\,NH_4Cl.$$

Ferrous salts in this respect are similar to those of magnesium (cf. p. 98). In the presence of ammonium chloride the reaction takes place in the direction from right to left; ammonia, therefore, causes no precipitation with ferrous salts out of contact with the air, provided sufficient ammonium chloride is present. On exposure to the air, however, a turbidity is soon formed, green at first, then almost black, and finally becoming brown. The small amount of ferrous hydroxide contained in the solution is oxidized by the air, forming at first black ferrous-ferric hydroxide and finally brown ferric hydroxide.

2. **Potassium** and **Sodium Hydroxides** produce, if air is excluded, complete precipitation of white ferrous hydroxide,

$$Fe^{++} + 2\,OH^- \rightarrow \mathbf{Fe(OH)_2},$$

which is quickly oxidized by the air into ferric hydroxide. The oxidation takes place immediately upon the addition of sodium peroxide:

$$2\,Fe^{++} + Na_2O_2 + 2\,OH^- + 2\,H_2O \rightarrow \mathbf{2\,Fe(OH)_3} + 2\,Na^+.$$

3. **Hydrogen Sulfide** produces no precipitation in acid solutions of ferrous salts; in dilute neutral solutions a small amount of black ferrous sulfide is precipitated; but if the solution contains *considerable alkali acetate*, hydrogen sulfide precipitates more of the iron as ferrous sulfide (but not all of it), in spite of the fact that ferrous sulfide is readily soluble in acetic acid. This interesting fact is an instructive illustration of the law of chemical mass action.

The table on p. 22 states that 3.4×10^{-8} g. of ferrous sulfide dissolves in a liter of water. This small quantity exists in solution almost entirely as Fe^{++} and S^{--} ions. $\mathbf{FeS} \rightleftarrows Fe^{++} + S^{--}$. When acetic acid, which is a much stronger acid than hydrogen sulfide (cf. p. 10), is added to the solution, equilibrium has to be established between its hydrogen ions and the dissolved sulfide ions, $2H^+ + S^{--} \rightleftarrows H_2S$, and, as a result of the formation of non-ionized hydrogen sulfide, the solution no longer contains enough sulfur ions to reach the value of the solubility product of FeS; to restore the equilibrium between FeS and its ions, more of the solid must dissolve. If, moreover, the solution is boiled, the hydrogen sulfide escapes as a gas as soon as it is formed. Consequently it is impossible to arrive at a state of equilibrium until all of the ferrous sulfide has dissolved. The solution is accomplished by means of hydrogen ions:

$$\mathbf{FeS} + 2\,H^+ \rightleftarrows Fe^{++} + H_2S\uparrow.$$

On the other hand, if the ionization of the acetic acid is repressed by adding an alkali acetate to the solution (cf. p. 47), and the concentration of the hydrogen sulfide is made as large as possible by keeping the solution saturated with the gas, the reaction will take place in the reverse direction and some of the iron will be precipitated as ferrous sulfide.

4. **Ammonium Sulfide** precipitates iron completely as black ferrous sulfide:

$$FeCl_2 + (NH_4)_2S = 2\,NH_4Cl + \mathbf{FeS},$$

which is readily soluble in acids with evolution of hydrogen sulfide. In moist air it turns slightly brown, a part of the sulfur separates out, and a basic ferric sulfate is formed.

5. **Alkali Carbonates** precipitate the white carbonate,

$$FeCl_2 + Na_2CO_3 = 2\,NaCl + \mathbf{FeCO_3},$$

which in contact with the air becomes green, then brown:

$$\mathbf{4\,FeCO_3} + 6\,H_2O + O_2 = 4\,CO_2\uparrow + \mathbf{4\,Fe(OH)_3},$$

being converted into ferric hydroxide with loss of carbonic anhydride.

Ferrous carbonate, like calcium carbonate (cf. p. 109), is soluble in carbonic acid, forming ferrous bicarbonate:

$$FeCO_3 + H_2CO_3 = FeH_2(CO_3)_2,$$

a compound which is found in many natural waters, but which, like the normal carbonate, is decomposed by atmospheric oxygen with separation of ferric hydroxide:

$$4\,FeH_2(CO_3)_2 + 2\,H_2O + O_2 = 8\,CO_2\uparrow + 4\,Fe(OH)_3.$$

Consequently a mineral water which contains ferrous bicarbonate, if allowed to stand in contact with the air, will become turbid, owing to the deposition of ferric hydroxide. To prevent this, the bottle must be filled with water and tightly corked, so that no trace of air can get in. Ferric hydroxide is insoluble in carbonic acid.

6. **Potassium Cyanide** precipitates yellowish-brown ferrous cyanide,

$$Fe^{++} + 2\,CN^- \rightarrow Fe(CN)_2,$$

which is soluble in excess of the reagent, forming potassium ferrocyanide:

$$Fe(CN)_2 + 4\,CN^- \rightarrow [Fe(CN)_6]^{--}.$$

The complex ferrocyanide anion is in equilibrium, to be sure, with simple ferrous cations, but the quantity of the latter present in the aqueous solution of a ferrocyanide is so small that none of the above reactions characteristic of ferrous ions can be obtained with it. Many other similar complex cyanide anions are known; thus, the cyanides of silver, nickel, iron (ferrous and ferric), and cobalt all dissolve in potassium cyanide, forming the following complex ions: $[Ag(CN)_2]^-$, $[Ni(CN)_4]^{--}$, $[Fe(CN)_6]^{---}$, $[Fe(CN)_6]^{--}[Co(CN)_6]^{---}$. The acids are:

$H[Ag(CN)_2]$, $H_2[Ni(CN)_4]$, $H_3[Fe(CN)_6]$, $H_4[Fe(CN)_6]$, $H_3[Co(CN)_6]$.

It is possible, as a matter of fact, to isolate the last three acids, though the two former have never been prepared; they immediately break down into metallic cyanide and hydrocyanic acid, just as carbonic acid is decomposed into water and carbon dioxide.

With iron, therefore, there are two series of complex cyanogen compounds, the ferrocyanides and the ferricyanides. The ferrocyanic derivatives contain the quadrivalent ferrocyanide anion and the ferricyanides contain the trivalent ferricyanide anion.

Potassium ferrocyanide, $K_4[Fe(CN)_6]$, is often called *yellow prussiate of potash*, and potassium ferricyanide, $K_3[Fe(CN)_6]$, is called *red prussiate of potash*. The solubility of the alkali and alkaline-earth salts, and

the insolubility and color of the salts of the heavy metals (especially with both ferric and ferrous iron), are very characteristic of ferro- and ferricyanides.

7. **Potassium Ferrocyanide,** $K_4[Fe(CN)_6]$, produces in solutions of ferrous salts, *with complete exclusion of air*, a *white* precipitate of *potassium ferrous ferrocyanide* or of *ferrous ferrocyanide*, depending upon whether one or two molecules of ferrous salt react with one molecule of potassium ferrocyanide:

$$K_4[Fe(CN)_6] + FeSO_4 = K_2SO_4 + \mathbf{K_2Fe[Fe(CN)_6]}$$

$$K_4[Fe(CN)_6] + 2\,FeSO_4 = 2\,K_2SO_4 + \mathbf{Fe_2[Fe(CN)_6]}$$

Although both of the above salts are white, a *light-blue* color is almost always obtained, because the precipitate is immediately oxidized somewhat by the air, forming the *ferric* salt of hydroferrocyanic acid (Prussian blue):

$$6\,Fe_2[Fe(CN)_6] + 6\,H_2O + 3\,O_2 = 2\,\underset{\text{Prussian blue}}{\mathbf{Fe_4[Fe(CN)_6]_3}} + 4\,\mathbf{Fe(OH)_3}.$$

8. **Potassium Ferricyanide,** $K_3[Fe(CN)_6]$, added to solutions of ferrous salts produces a dark blue precipitate (Turnbull's blue) consisting of ferrous ferricyanide mixed with potassium-ferric ferrocyanide:

$$2\,K_3[Fe(CN)_6] + 3\,FeCl_2 = 6\,KCl + \mathbf{Fe_3[Fe(CN)_6]_2}$$

and

$$K_3[Fe(CN)_6] + FeCl_2 = \mathbf{KFe^{+++}[Fe(CN)_6]^{=}} + 2\,KCl.$$

In other words the ferricyanide acts both as a precipitant and as an oxidizing agent * and a blue color results whenever iron is present in the cation in a state of oxidation different from that of the iron present in the complex anion. The ferricyanide ion is a strong oxidizing agent and in alkaline solution readily oxidizes ferrous hydroxide to ferric hydroxide. Turnbull's blue is not very soluble in acid solutions, but is decomposed by treatment with caustic alkali, all of the complex anion being in the form of ferrocyanide:

$$Fe_3{}^{++}[Fe(CN)_6]_2{}^{---} + 8\,KOH = 2\,K_4[Fe(CN)_6] + 2\,\mathbf{Fe(OH)_3} + \mathbf{Fe(OH)_2},$$

$$K^{+}Fe^{+++}[Fe(CN)_6]^{=} + 3\,KOH = K_4[Fe(CN)_6] + \mathbf{Fe(OH)_3}.$$

9. **Potassium Thiocyanate** gives no reaction with ferrous salts (note difference from ferric salts).

As has been stated, ferrous salts are oxidized by the air to ferric salts; thus ferrous sulfate is gradually changed into brown, basic ferric sulfate,

$$4\,FeSO_4 + O_2 = 2\,[Fe_2O\cdot(SO_4)_3],$$

which is insoluble in water. Consequently it often happens that ferrous sulfate will not dissolve in water to a clear solution, but gives a brown, turbid solution, becoming clear on the addition of acid, the basic ferric salt being changed to a soluble neutral salt:

$$Fe_2O\cdot(SO_4)_3 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O.$$

* Cf. Erich Müller, *J. pr. Chem.*, **84** (1911), 353.

Such a solution, which then contains ferric ions, reacts with potassium thiocyanate (cf. p. 158). To free the solution from ferric salt, it may be boiled with metallic iron, out of contact with air, whereby the ferric salt is changed into ferrous salt:

$$Fe_2(SO_4)_3 + Fe = 3\,FeSO_4.$$

By means of strong oxidizing agents, ferrous salts can be quickly and completely changed into ferric salts, as was shown in the introduction (cf. pp. 29–33).

10. **Ammonium Thioacetate,*** CH_3COSNH_4, gives no reaction in an acid solution of a ferrous salt but ferrous sulfide is precipitated in an alkaline solution:

$$CH_3COS^- + Fe^{++} + 2\,OH^- \rightarrow C_2H_3O_2^- + \mathbf{FeS} + H_2O.$$

Sodium thiosulfate, however, does not cause precipitation.

11. **α-Nitroso-β-naphthol,** $C_{10}H_6(NO)OH$, gives a green coloration with dilute solutions of ferrous salts and, on standing, a flocculent precipitate of ferrous nitroso-β-naphthol is formed. Hydrogen ions prevent this reaction, even the small quantity formed by the hydrolysis of a ferric salt. Sodium acetate must be added in the latter case. The precipitate oxidizes easily to the corresponding ferric compound.

12. **Dimethylglyoxime,** $(CH_3)_2C_2N_2(OH)_2$, added to a ferrous solution containing tartaric acid gives, upon the addition of ammonia, a deep reddish coloration. As the ferrous iron oxidizes, the color fades. This reaction is sensitive.

Detection of Ferrous Oxide in the Presence of Metallic Iron

Treat the mixture with a large excess of a neutral solution of mercuric chloride and heat on the water-bath; the metallic iron goes into solution as ferrous chloride:

$$2\,HgCl_2 + \mathbf{Fe} = FeCl_2 + \mathbf{Hg_2Cl_2}.$$

Filter off the residue and test the filtrate with potassium ferricyanide; a precipitate of Turnbull's blue shows that metallic iron was originally present.

Wash the residue with cold water, until all the ferrous chloride has been dissolved, and then treat it with dilute hydrochloric acid. If the solution now gives a precipitate of Turnbull's blue with potassium ferricyanide, ferrous oxide was present.

If hydrogen is given off, some metallic iron is still present; the experiment must be repeated and the mixture given a longer treatment with $HgCl_2$ solution.

* Acetic acid is $HC_2H_3O_2$ or, as the organic chemist prefers, $CH_3CO \cdot OH$. Thioacetic acid has the same formula except that the last oxygen is replaced by sulfur. It is made by the action of phosphoric pentasulfide upon glacial acetic acid. The substance has an unpleasant odor and is fairly expensive. SCHIFF and TARUGI (*Z. anal. Chem.*, **34**, 456) have recommended the use of a faintly ammoniacal solution of the ammonium salt instead of hydrogen sulfide. It is a very effective precipitant of sulfides. Sodium thiosulfate will give sulfide precipitates with many cations but its sulfur atom with the negative valence of two is less accessible than in thioacetic acid.

B. Ferric Compounds

Ferric oxide, Fe_2O_3, is reddish brown, becomes grayish black on strong ignition, but on being pulverized appears red again.

Ferric salts are usually yellow or brown, but ferric ammonium alum is pale violet. Ferric salts are yellowish brown in aqueous solution, and the solution reacts acid (hydrolysis). Dilution and warming favor the hydrolysis, so that all strongly diluted ferric salts deposit basic salts on being boiled:

$$Fe_2(SO_4)_3 + H_2O \rightleftarrows \mathbf{Fe_2(SO_4)_2O} + H_2SO_4.$$

With ferric salts of the weaker acids, often all of the iron is precipitated as a basic salt; thus the acetate, on being boiled in a dilute solution, reacts as follows:

$$Fe(C_2H_3O_2)_3 + 2\,H_2O \rightleftarrows \mathbf{Fe(OH)_2(C_2H_3O_2)} + 2\,HC_2H_3O_2.$$

By the addition of acid all basic salts may be changed back into neutral salts.

Reactions of Ferric Salts in the Wet Way

1. **Ammonia** precipitates brown, gelatinous ferric hydroxide:

$$Fe^{+++} + 3\,OH^- \rightarrow \mathbf{Fe(OH)_3}.$$

The solubility product of ferric hydroxide is so small (cf. p. 22) that it is precipitated completely even in the presence of ammonium salts; it is readily soluble in acids. On ignition it loses water and is changed to oxide, which is very difficultly soluble in dilute acids. It is best brought into solution by long-continued heating below the boiling point with concentrated hydrochloric acid.

In spite of the slight solubility of ferric hydroxide, it is not formed in the presence of many organic substances with which ferric ions unite to form complexes. (See § 6, below.)

2. **Potassium** and **Sodium Hydroxide** also precipitate ferric hydroxide.

3. **Sodium Carbonate** produces a brown precipitate of basic carbonate, which at the boiling temperature is completely decomposed hydrolytically into hydroxide and carbon dioxide:

$$2\,FeCl_3 + 3\,Na_2CO_3 + 3\,H_2O = 2\,\mathbf{Fe(OH)_3} + 6\,NaCl + 3\,CO_2\uparrow.$$

4. **Zinc Oxide** and **Mercuric Oxide** also precipitate the iron as hydroxide:

$$2\,FeCl_3 + 3\,\mathbf{ZnO} + 3\,H_2O = 3\,ZnCl_2 + 2\,\mathbf{Fe(OH)_3}.$$

This reaction is frequently used in quantitative analysis.

5. **Sodium Phosphate** precipitates yellowish-white ferric phosphate:

$$FeCl_3 + 2\,Na_2HPO_4 = 3\,NaCl + NaH_2PO_4 + \mathbf{FePO_4}.$$

Ferric phosphate is insoluble in acetic acid, but readily soluble in mineral acids. The precipitation of iron with sodium hydrogen phosphate is consequently only complete when a large excess of the precipitant is employed, or when sodium acetate is added:

$$FeCl_3 + Na_2HPO_4 + NaC_2H_3O_2 = 3\,NaCl + HC_2H_3O_2 + \mathbf{FePO_4}.$$

In this last case all the iron and all the phosphoric acid are precipitated. The reaction is often used to precipitate phosphoric acid quantitatively. An excess of the disodium phosphate will also cause complete precipitation of iron as phosphate, if the phosphate solution is previously exactly neutralized with ammonia:

$$Na_2HPO_4 + NH_4OH = H_2O + Na_2NH_4PO_4,$$

and

$$Na_2NH_4PO_4 + FeCl_3 = 2\,NaCl + NH_4Cl + \mathbf{FePO_4}.$$

If, however, an excess of sodium phosphate and ammonia is added to the iron solution, the precipitation of iron is incomplete, because the ferric phosphate dissolves in the excess of sodium phosphate, in the presence of ammonia (or ammonium carbonate), with a brown color and formation of a complex salt.

Ferric phosphate is transformed by ammonia into a brown basic phosphate, and by potassium hydroxide almost completely into ferric hydroxide and potassium phosphate; while by *fusion* with caustic alkali or alkali carbonate it is completely decomposed.

If alkaline earth ions are present, an excess of ammonia completely changes ferric phosphate to ferric hydroxide and alkaline earth phosphate is precipitated.

6. **Alkali Acetates** produce in cold, neutral solutions a dark-brown coloration, and on boiling the dilute solution all of the iron separates as basic acetate:

$$FeCl_3 + 3\,NaC_2H_3O_2 = 3\,NaCl + Fe(C_2H_3O_2)_3 \text{ (in the cold)},$$

$$Fe(C_2H_3O_2)_3 + 2\,H_2O = 2\,HC_2H_3O_2 + \mathbf{Fe(OH)_2C_2H_3O_2} \text{ (on boiling)}.$$

The presence of organic hydroxy-acids (tartaric, malic, citric, etc.) and of polyatomic alcohols (glycerol, erythritol, mannitol, sugars, etc.) prevent all of the above-mentioned reactions, because complex salts are formed in which the iron is present in the form of a complex anion (cf. aluminium, p. 135).

7. **Potassium Thiocyanate,** KCNS, produces in solutions of ferric salts a blood-red coloration:

$$Fe^{+++} + 3\,CNS^- \rightleftarrows Fe(CNS)_3.$$

This action is reversible; the red color of the slightly ionized ferric thiocyanate being most intense when an excess of ferric salt, or of potassium thiocyanate, is present.

If the solution is shaken with ether, the $Fe(CNS)_3$ goes into the ether. Ferric thiocyanate combines readily with potassium thiocyanate, forming complex potassium ferrithiocyanate:

$$Fe(CNS)_3 + 3\,KCNS = K_3[Fe(CNS)_6]\,*$$

analogous to potassium ferricyanide, $K_3[Fe(CN)_6]$.

The complex salt is insoluble in ether, the $Fe(CNS)_3$ only being soluble therein; so that the red color is due to the formation of the ferric thiocyanate and not to the complex salt.

This reaction is extremely sensitive, but cannot always be relied on. In ferric solutions which are more or less red by the presence of ferric-acetate-complex ions, the red color of ferric thiocyanate can be seen only when considerable hydrochloric acid is added. Similarly if the solution contains oxalic, tartaric, citric, malic, iodic, phosphoric, arsenic or hydrofluoric acid, the red color is not obtained except when nitric acid is present. The test must then be made in the cold solution because hot nitric acid decomposes the sulfocyanate ion and, at the same time, the nitrite ion on its part gives a red coloration with sulfocyanate; this nitrite color disappears, however, upon heating with a little alcohol which does not affect ferric thiocyanate. The sensitiveness of the reaction can be increased somewhat by adding an excess of freshly-prepared potassium thiocyanate solution and shaking with ether. In the presence of mercuric chloride the red color disappears entirely; the mercuric chloride reacts with the ferric thiocyanate, forming a colorless, soluble mercuric double salt, which is ionized even less than ferric thiocyanate:

$$2\,Fe(CNS)_3 + 6\,HgCl_2 = 2\,FeCl_3 + 3\,[Hg(CNS)_2 \cdot HgCl_2].$$

8. **Potassium Ferrocyanide,** $K_4[Fe(CN)_6]$ produces in neutral or acid solutions of ferric salts an intense blue precipitation of Prussian blue:

$$3\,[Fe(CN)_6]^{----} + 4\,Fe^{+++} \rightarrow \mathbf{Fe_4[Fe(CN)_6]_3}.$$

Prussian blue, the ferric salt of ferrocyanic acid, is insoluble in water, but soluble in oxalic acid and in an excess of potassium ferrocyanide; the solution thus obtained is a deep blue and is used as bluing and as blue ink. The blue solution obtained with a ferric salt and an excess of potassium ferrocyanide contains colloidal $KFe[Fe(CN)_6] \cdot H_2O$, which can be *salted out* by the addition of a considerable quantity of electrolyte such as alkali chloride, sulfate or nitrate. Prussian blue is also soluble in concentrated hydrochloric acid, but is precipitated again on dilution. As the ferric salt of ferrocyanic acid it behaves like other ferric salts to the hydroxides of the alkalies; ferric hydroxide and the alkali salt of hydroferrocyanic acid being formed:

$$\mathbf{Fe_4[Fe(CN)_6]_3} + 12\,OH^- \rightarrow \mathbf{4\,Fe(OH)_3} + 3\,[Fe(CN)_6]^{----}.$$

9. **Potassium Ferricyanide,** $K_3[Fe(CN)_6]$, produces no precipitation in solutions of ferric salts, only a brown coloration (differing from ferrous salts):

$$[Fe(CN)_6]^{---} + Fe^{+++} \rightleftarrows 2\,Fe(CN)_3.$$

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* $K_3[Fe(CNS)_6] + 4\,H_2O$. Cf. ROSENHEIM, *Z. anorg. Chem.*, **27** (1901), 208.

10. **Ammonium Sulfide,** added to a solution of a ferric salt, gives a precipitate of ferric sulfide, Fe_2S_3,

$$2\,Fe^{+++} + 3\,S^{--} \rightarrow \mathbf{Fe_2S_3},$$

which is soluble in cold, dilute hydrochloric acid, forming ferrous chloride and sulfur:

$$\mathbf{Fe_2S_3} + 4\,H^+ \rightarrow 2\,Fe^{++} + 2\,H_2S\uparrow + \mathbf{S}.$$

The fact that Fe_2S_3 is precipitated, and not FeS as commonly believed, was proved by H. N. Stokes * who decomposed it out of contact with air by zinc-ammonium oxide and obtained white ZnS and red $Fe(OH)_3$. L. Gedel † has also shown that hydrogen sulfide passed into a solution of ferric chloride made alkaline with ammonia gives Fe_2S_3. If, however, the solution is acid, hydrogen sulfide or ammonium sulfide reduces the ion before any precipitate is formed.

11. **Hydrogen Sulfide** in acid solutions reduces ferric salts to ferrous salts, with separation of sulfur:

$$2\,Fe^{+++} + H_2S \rightarrow 2\,Fe^{++} + 2\,H^+ + \mathbf{S}.$$

Besides hydrogen sulfide, many other substances (metals, stannous chloride, sulfurous acid, hydriodic acid, etc.) will reduce ferric salts, as was shown on pp. 35, 36.

12. **Ether** when shaken with a solution of ferric chloride in 6 N hydrochloric acid dissolves most of the ferric chloride. By separating the ether with the aid of a separatory funnel, and repeating the operation, nearly all of the iron can be removed from the aqueous solution. (Cf. p. 17.)

13. **Cupferron,** the ammonium salt of phenylnitrosohydroxylamine, $C_6H_5NO\cdot NONH_4$, precipitates red $(C_6H_5NO\cdot NO)_3Fe$, which is soluble in ether, insoluble in acids, and converted into $Fe(OH)_3$ by treatment with ammonia.

14. **Sodium Thiosulfate,** $Na_2S_2O_3$, colors neutral ferric solutions a violet red, but the color disappears quickly and the solution then contains *ferrous* salt and *sodium tetrathionate:*

$$2\,Na_2S_2O_3 + 2\,FeCl_3 = 2\,NaCl + 2\,FeCl_2 + Na_2S_4O_6.$$

The composition of the violet-red substance which is first formed is unknown; perhaps it is ferric *thiosulfate.*

15. **Ammonium Thioacetate,** $NH_4C_2H_3OS$, reduces ferric salts in acid solutions and precipitates ferrous sulfide if alkali is present:

$$2\,Fe^{+++} + C_2H_3OS^- + H_2O \rightarrow 2\,Fe^{++} + HC_2H_3O_2 + H^+ + \mathbf{S},$$

$$2\,Fe^{+++} + 3\,C_2H_3OS^- + 6\,OH^- \rightarrow 2\,\mathbf{FeS} + 3\,C_2H_3O_2^- + 3\,H_2O + \mathbf{S}.$$

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* *J. Am. Chem. Soc.*, **29** (1907), 304.

† *Ueber Schwefeleisen*, Karlsruhe, (1905).

16. **α-Nitroso-β-naphthol,** $C_{10}H_6(NO)OH$, gives a voluminous, brownish-black precipitate of ferric nitroso-β-naphthol, $(C_{10}H_6NO \cdot O)_3Fe$, in neutral or slightly acid solutions.

17. **Cobalt Chloride** dissolved in concentrated hydrochloric acid gives a deep blue solution. If a little of this blue liquid is added to a solution containing a small quantity of ferric ions, a green color is obtained. Venable has recommended this reaction as a test for ferric ions in acids or for detecting ferric ions in the presence of ferrous ions.

As we have seen, there exist a number of iron compounds which contain the metal as a complex ion, so that it cannot be detected by the ordinary reagents. The complex hydroxy-organic compounds, as well as the ferro- and ferricyanides, belong to this class of compounds.

If it is a question of proving the presence of iron in such a compound, a different method should be used in the case of an organic hydroxy-compound from that in the case of a ferro- or ferricyanide.

If organic substances are present, the iron is precipitated as sulfide by means of ammonium sulfide; or the organic matter is first removed by ignition, whereby metallic iron, oxides of iron and carbon are obtained.

In case we have a ferro- or ferricyanide, the iron cannot even be precipitated by means of ammonium sulfide; the compound must be completely destroyed before it will be possible to detect the presence of iron by any of the ordinary methods.

This may be accomplished (*a*) by ignition, (*b*) by fusion with potassium carbonate or sodium carbonate, or (*c*) by heating strongly with concentrated sulfuric acid.

(*a*) *Decomposition by Ignition.* — The ferrocyanides and ferricyanides are all decomposed by ignition but the products of the decomposition vary according to the conditions. The alkali salts yield alkali cyanide, iron carbide and nitrogen but hydrocyanic acid, carbon dioxide, ammonia and cyanogen are also obtained to some extent. The reaction is reversible and it is possible to utilize the reversed reaction for the fixation of atmospheric nitrogen; iron, carbon, alkali carbonate and nitrogen are heated together and some alkali ferrocyanide is obtained.

After the ignition of the complex cyanide, extract the residue with water, whereby any alkali cyanide is removed. Filter and treat the residue with dilute hydrochloric acid; iron and iron carbide dissolve as ferrous chloride, hydrocarbons are evolved, and some carbon remains undissolved.

(*b*) *Decomposition by Means of Fusion with Potassium Carbonate.* — Mix the substance with an equal amount of the carbonate and heat in a porcelain crucible until a quiet fusion is obtained. By this means a mixture of potassium cyanide and potassium cyanate (both soluble in water) is formed in the presence of metallic iron:

$$K_4[Fe(CN)_6] + K_2CO_3 = 5\,KCN + KCNO + CO_2\uparrow + Fe.$$

Extract the melt with water, filter and dissolve the iron in hydrochloric acid.

(*c*) *Decomposition by Heating with Concentrated Sulfuric Acid.* — By heating with concentrated sulfuric acid all complex cyanogen compounds may be decomposed. By this means the metal present is changed into sulfate, the nitrogen of the cyanogen into ammonium sulfate, while the carbon of the cyanogen escapes as carbon monoxide:

$$K_4[Fe(CN)_6] + 6\,H_2SO_4 + 6\,H_2O = 2\,K_2SO_4 + FeSO_4 + 3\,(NH_4)_2SO_4 + 6\,CO\uparrow,$$

$$2\,K_3[Fe(CN)_6] + 12\,H_2SO_4 + 12\,H_2O = 3\,K_2SO_4 + Fe_2(SO_4)_3 + 6\,(NH_4)_2SO_4 + 12\,CO\uparrow.$$

The treatment with concentrated sulfuric acid is best accomplished in a porcelain crucible placed in an inclined position over the flame, and the flame directed against the upper part of the crucible. Continue heating until fumes of sulfuric acid cease to come off. Treat the residue, which consists of an alkali sulfate and anhydrous ferrous or ferric sulfate, with a little concentrated sulfuric acid, heat gently, and add water little by little. In this way the sulfate is readily brought into solution.

Reactions in the Dry Way

The borax (or sodium metaphosphate) bead, containing a small amount of an iron salt, is yellow while hot and colorless when cold after being heated in the oxidizing flame, and pale green after being heated in the reducing flame. When strongly saturated, however, the bead obtained with the oxidizing flame is brown while hot, yellow when cold; and after heating in the reducing flame it becomes bottle-green.

Heated on charcoal with soda before the blowpipe, all iron compounds leave a gray particle of metallic iron, which is usually difficult to see, but can be separated from the charcoal by means of the magnet. The reduction on the charcoal stick, as described on p. 66, is a much more delicate test.

URANIUM, U. At. Wt. 228.2

Sp. Gr. = 18.33. M. Pt. = 2500° (?)

Occurrence. — Uranium occurs in nature chiefly in the mineral pitch-blende, U_3O_8; but it is also found in a few rare minerals, uranite, $(UO_2)_2Cu(PO_4)_2 + 8\,H_2O$; samarskite (a niobite of iron, yttrium, cerium, and erbium with varying amounts of uranium); and liebigite, $U(CO_3)_2 \cdot 2\,CaCO_3 + 10\,H_2O$.

Klaproth showed, in 1789, that the mineral pitch-blende contained a new metal, which he called uranium. By heating the oxide with reducing agents he obtained a brown, almost copper-red, substance, which he took to be the metal, and it indeed does behave like a metal, dissolving in acids in contact with the air, forming yellowish-green salts.

It was not until 1842 that it was shown by Péligot that this reddish-brown body was not the metal uranium, but its dioxide. The hexavalent metal itself was obtained by Péligot, as a gray powder, by reducing the tetrachloride with sodium.

Out of contact with the air, uranium dioxide (uranyl) dissolves in strong acids, forming *uranous* salts:

$$UO_2 + 4\,HCl = 2\,H_2O + UCl_4, \quad UO_2 + 2\,H_2SO_4 = 2\,H_2O + U(SO_4)_2.$$

The uranous salts are extremely unstable, and on being exposed to the air change rapidly, forming *uranyl* salts which contain the bivalent UO_2 group:

$$2\,UCl_4 + O_2 + 2\,H_2O \rightarrow 2\,UO_2Cl_2 + 4\,HCl,$$

$$2\,U(SO_4)_2 + O_2 + 2\,H_2O = 2\,UO_2SO_4 + 2\,H_2SO_4.$$

Only the reactions of the uranyl salts will be described in this book.

Besides uranyl (or uranium dioxide) uranium forms a trioxide, UO_3, which can be regarded as uranyl oxide, UO_2O. It dissolves in acids, forming uranyl salts:

$$UO_3 + 2\,HCl = UO_2Cl_2 + H_2O.$$

By igniting the oxides of uranium in air, dark-green urano-uranic oxide, U_3O_8 or $(2\,UO_3 \cdot UO_2)$, is obtained, which out of contact with the air dissolves in strong acids, forming a mixture of uranous and uranyl salts:

$$(2\,UO_3 \cdot UO_2) + 4\,H_2SO_4 = 2\,UO_2SO_4 + U(SO_4)_2 + 4\,H_2O.$$

By dissolving in aqua regia, uranyl chloride is obtained:

$$3\,U_3O_8 + 18\,HCl + 2\,HNO_3 = 9\,UO_2Cl_2 + 2\,NO + 10\,H_2O.$$

All uranyl compounds are colored yellow or yellowish green. Most of them are soluble in water, but the oxides, the sulfide, phosphate, and uranates are insoluble. In mineral acids all uranium compounds are soluble, with the exception of the ferrocyanide.

Reactions of Uranyl Compounds in the Wet Way

1. **Potassium Hydroxide** precipitates yellow amorphous potassium uranate. Uranyl hydroxide, $UO_2(OH)_2$, is first formed and changes into uranic acid, $H_2U_2O_7$, of which the alkali salts are insoluble:

$$2\,UO_2Cl_2 + 6\,KOH \rightarrow \mathbf{K_2U_2O_7} + 4\,KCl + 3\,H_2O.$$

2. **Ammonia** precipitates yellow, amorphous ammonium uranate:

$$2\,UO_2(NO_3)_2 + 6\,NH_4OH \rightarrow \mathbf{(NH_4)_2U_2O_7} + 4\,NH_4NO_3 + 3\,H_2O.$$

The alkali uranates are soluble in alkali carbonates, particularly in ammonium carbonate, with the formation of complex salts:

$$\mathbf{(NH_4)_2U_2O_7} + 6\,(NH_4)_2CO_3 + 3\,H_2O \rightarrow 2\,(NH_4)_4[UO_2(CO_3)_3] + 6\,NH_4OH.$$

Consequently, in the presence of sufficient alkali carbonate, ammonia fails to precipitate uranium. Tartaric and citric acids (and other organic substances) also prevent the precipitation with ammonia and caustic alkalies, as with iron, chromium, and aluminium.

3. **Sodium Carbonate** produces in concentrated solutions an orange-yellow precipitate of sodium uranyl carbonate:

$$UO_2(NO_3)_2 + 3\,Na_2CO_3 = 2\,NaNO_3 + \mathbf{Na_4[UO_2(CO_3)_3]}.$$

Sodium uranyl carbonate is soluble in *considerable* water, so that *no precipitate is formed from dilute solutions. It is still more soluble in alkali carbonate solution, particularly in a bicarbonate solution.* From such solutions sodium hydroxide precipitates sodium uranate, but ammonia produces no precipitation.

4. **Barium Carbonate** precipitates in the cold all of the uranium, probably as barium uranyl carbonate:

$$UO_2(NO_3)_2 + 3\,BaCO_3 = Ba(NO_3)_2 + \mathbf{Ba_2[UO_2(CO_3)_3]}.$$

5. **Ammonium Sulfide** precipitates brown uranyl sulfide,

$$UO_2(NO_3)_2 + (NH_4)_2S = 2\,NH_4NO_3 + \mathbf{UO_2S},$$

soluble in dilute acids and in ammonium carbonate:

$$\mathbf{UO_2S} + 3\,(NH_4)_2CO_3 = (NH_4)_2S + (NH_4)_4[UO_2(CO_3)_3].$$

Ammonium sulfide, therefore, produces no precipitate in solutions of uranyl salts in the presence of ammonium carbonate.

By boiling the solution of uranium salt to which ammonium sulfide has been added, the uranyl sulfide decomposes into sulfur and black uranous oxide, UO_2, and the latter is insoluble in an excess of the ammonium sulfide and in ammonium carbonate solution. If uranyl sulfide stands for some time in contact with an excess of ammonium sulfide, it is gradually changed into a red substance with access of air or to a black substance if air is excluded: the reaction is probably due to the formation of ammonium thiosulfate.

6. **Sodium Phosphate** precipitates yellowish-white uranyl phosphate

$$UO_2(NO_3)_2 + Na_2HPO_4 \rightarrow 2\,NaNO_3 + \mathbf{UO_2HPO_4},$$

while, in the presence of ammonium acetate, uranyl ammonium phosphate is precipitated:

$$Na_2HPO_4 + UO_2(NO_3)_2 + NH_4C_2H_3O_2 \rightarrow$$
$$2\,NaNO_3 + HC_2H_3O_2 + \mathbf{UO_2 \cdot NH_4PO_4}.$$

Both precipitates are insoluble in acetic acid, but soluble in mineral acids.

7. **Potassium Ferrocyanide** produces a brown precipitate, or in very dilute solutions, a brownish-red coloration,

$$Fe(CN)_6^{--} + 2\,UO_2^{++} \rightarrow \mathbf{(UO_2)_2[Fe(CN)_6]}.$$

On addition of potassium hydroxide the brownish-red precipitate becomes yellow, owing to the formation of potassium uranate:

$$\mathbf{(UO_2)_2[Fe(CN)_6]} + 6\,KOH = K_4[Fe(CN)_6] + 3\,H_2O + \mathbf{K_2U_2O_7}.$$

(Distinction from cupric ferrocyanide.)

8. **Zinc,** in the presence of dilute sulfuric acid, reduces yellow uranyl salt to green uranous salt.

9. **Mercuric Oxide** suspension precipitates uranium completely by boiling the solution containing ammonium chloride. (Separation of uranium from strontium, calcium and alkali ions and less satisfactorily from barium ions.)

10. **Hydrogen Peroxide** precipitates yellowish uranium tetroxide, insoluble in hydrochloric acid. The presence of sulfate ions hinders the precipitation. The oxide dissolves in ammonium carbonate solution, giving a deep yellow solution. If the precipitate produced by hydrogen peroxide is dissolved in sulfuric acid and the solution is shaken with a little ether, the latter is colored blue.

11. **Sodium Peroxide** produces a yellow precipitate soluble in an excess of the reagent; the addition of alcohol then precipitates yellow sodium peruranate, $Na_4U_2O_8 \cdot 8\ H_2O$.

12. **Turmeric Paper** is colored brown by aqueous solutions of uranyl salts, especially the nitrate. The presence of considerable acid prevents the reaction.

Reactions in the Dry Way

The borax (or sodium metaphosphate) bead is yellow in the oxidizing flame and green in the reducing flame.

TITANIUM, Ti. At. Wt. 48.1

Sp. Gr. = 4.87. M. Pt. = 1900° (?)

Occurrence. — Titanium occurs in nature most frequently as the dioxide, rutile (tetragonal), anatase (tetragonal), and brookite (orthorhombic). Titanium is also found in the minerals perowskit, $CaTiO_3$, titanite, $CaSiTiO_5$, and ilmenite, $FeTiO_3$, as well as in many crystalline rocks. It is present in most rocks, but usually only in very small quantity.

Titanium itself is a gray metal, very similar to iron. On being heated in the air it burns brightly to white titanium oxide. The following oxides of titanium are known: Ti_2O_2, Ti_2O_3, TiO_2, TiO_3 or possibly $TiO_2 \cdot H_2O_2$.

The oxides Ti_2O_2 and Ti_2O_3 form violet-colored salts, which are readily changed by oxidizing agents into derivatives of TiO_2. The most important oxide is titanium dioxide, which is amphoteric and sometimes acts as a base and sometimes as an acid. The titanium dioxide as it occurs in nature (rutile, etc.) is insoluble in all acids. In order to bring it into solution it is best to fuse it with potassium pyrosulfate, whereby it is changed into titanium sulfate:

$$TiO_2 + 2\ K_2S_2O_7 = Ti(SO_4)_2 + 2\ K_2SO_4.$$

The melt is dissolved in cold water. It can also be dissolved by fusing with sodium carbonate and treating the melt with 6 N hydrochloric acid.

Titanium dioxide shows a pronounced amphoteric behavior. As the anhydride of a weak acid, it forms metatitanates (salts of H_2TiO_3). These salts are easy to prepare in the dry way, but in aqueous solution they are hydrolyzed and titanic acid, ($TiO_2 \cdot xH_2O$), is precipitated. As cation, quadrivalent titanium forms salts which are also easily hydrolyzed.

Titanium salts, containing bivalent titanium, are so easily oxidized that they have not been studied much.

Titanium with a valence of three forms a series of salts which are sometimes used as energetic reducing agents. The aqueous solutions are usually violet in color but can be changed into less stable green solutions, like chromium. The salts of trivalent titanium behave like iron and aluminium toward the common reagents. Titanium oxalate is yellowish red in color.

The analytical chemist is concerned chiefly with quadrivalent titanium. With increasing valence the basic character of the metal decreases. The salts of quadrivalent titanium are colorless. The tetrachloride, $TiCl_4$, boils at 136°; the tetrafluoride at 284°. The latter forms with hydrofluoric acid the complex fluortitanic acid, H_2TiF_6, which forms a difficultly soluble potassium salt, K_2TiF_6. The sulfate, $Ti(SO_4)_2$, shows a marked tendency to form basic salts, e.g. titanyl sulfate, $TiO \cdot SO_4$.

Reactions in the Wet Way

For these reactions a solution of titanium sulfate or of titanium hydroxide in hydrochloric acid may be used.

1. **Potassium Hydroxide** precipitates, in the cold, gelatinous *orthotitanic* acid,

$$Ti^{++++} + 4\,OH^- \rightarrow H_4TiO_4,$$

which is almost insoluble in an excess of the reagent, but readily soluble in mineral acids.

If the precipitation by potassium hydroxide takes place from a hot solution the titanium is precipitated as *metatitanic* acid,

$$Ti^{++++} + 4\,OH^- \rightarrow H_2O + H_2TiO_3,$$

which is difficultly soluble in dilute acids. By long digestion with concentrated hydrochloric or sulfuric acid it goes gradually into solution. By the ignition of both these titanic acids the anhydride

TiO_2 is obtained, which is only slightly soluble in concentrated hydrochloric acid, but readily soluble in hot concentrated sulfuric acid.

2. **Ammonia, Ammonium Sulfide,** and **Barium Carbonate** (like potassium hydroxide) precipitate, in the cold, orthotitanic acid, readily soluble in acids; and from hot solutions the difficultly soluble metatitanic acid.

$$TiCl_4 + 4\,NH_4OH = 4\,NH_4Cl + \mathbf{H_4TiO_4},$$

$$TiCl_4 + 2\,(NH_4)_2S + 4\,H_2O = 4\,NH_4Cl + 2\,H_2S\uparrow + \mathbf{H_4TiO_4},$$

$$TiCl_4 + 2\,BaCO_3 + 2\,H_2O = 2\,BaCl_2 + 2\,CO_2\uparrow + \mathbf{H_4TiO_4}.$$

3. **Alkali Acetates** precipitate on boiling all of the titanium as metatitanic acid:

$$Ti^{++++} + 4\,C_2H_3O_2^- + 3\,H_2O = 4\,HC_2H_3O_2 + \mathbf{H_2TiO_3}.$$

Titanium acetate is first formed, but it is completely decomposed hydrolytically by boiling the dilute solution.

4. **Water.** — Not only titanium acetate but all titanium salts are hydrolytically decomposed by water.

The ease with which soluble titanium salts undergo hydrolysis with the formation of insoluble titanic acid is the basis of the several methods for separating titanium from aluminium, iron, chromium, etc.; the oxides of these metals are fused with potassium pyrosulfate, the product of the fusion is dissolved in cold water,* and the solution is then heated to boiling. The titanium is completely precipitated as granular metatitanic acid, which can be readily filtered off, while the remaining metals remain in solution as sulfates:

$$Ti(SO_4)_2 + 3\,H_2O \rightleftarrows 2\,H_2SO_4 + H_2TiO_3.$$

As this reaction, like all hydrolytic decompositions, is reversible, it is evident that, in order to make the precipitation of the metatitanic acid complete, the *amount of free acid present should be kept small,*† *considerable water should be used, and the solution kept hot while filtering.*

In order to precipitate titanic acid from a solution according to this method, the concentrated solution is treated with sodium carbonate in the cold until a slight permanent precipitate of $Ti(OH)_4$ is obtained, sulfuric acid is added drop by drop until the precipitate is just dissolved, considerable water is added (300 to 500 cc. of water should be used for each 0.1 gm. TiO_2) and the solution kept at the boiling temperature for one hour. The granular metatitanic acid thus obtained is easy to filter as long as free acid is present. On being washed with pure water a turbid filtrate is always obtained; a little dilute sulphuric acid should therefore be added to the wash-water.

With the separation of titanium according to the above-described method, a play of colors will be observed in the bottom of the glass beaker or flask which is very characteristic of titanic acid.

* Solution takes place much more quickly if the liquid is kept in constant motion, e.g., by conducting a current of air through it.

† If too little acid is present, however, iron and aluminium will precipitate.

The presence of tartaric acid, citric acid, and many other organic compounds prevents the above reactions. In such a case the organic substance must be first destroyed either by ignition or by oxidation with potassium permanganate (see pp. 137 and 161), the titanium dioxide dissolved in sulfuric acid and precipitated according to any of the above methods.

5. **Potassium Ferrocyanide** produces in slightly acid solutions a brown precipitate.

6. **Tannin** produces a brown precipitate, which soon becomes orange.

7. **Sodium Thiosulfate** precipitates in boiling solutions all of the titanium as metatitanic acid:

$$TiCl_4 + 2\,Na_2S_2O_3 + H_2O = 4\,NaCl + 2\,S + 2\,SO_2\uparrow + \mathbf{H_2TiO_3}.$$

8. **Sodium Phosphate** precipitates basic titanium phosphate,

$$TiCl_4 + 3\,Na_2HPO_4 + H_2O = 4\,NaCl + 2\,NaH_2PO_4 + \mathbf{Ti(PO_4)(OH)},$$

soluble in mineral acids, insoluble in acetic acid.

9. **Hydrogen Peroxide.** — If hydrogen peroxide is added to a slightly acid solution of titanium sulfate, the solution is colored orange red, except in the presence of small amounts of titanium, when the color is light yellow. This reaction, which depends upon the formation of TiO_3, or possibly $TiO_2 \cdot H_2O_2$, is exceedingly delicate, and is especially suitable for the detection of titanium in rocks. Vanadic acid behaves similarly with hydrogen peroxide.

If a solution of titanium sulfate is treated with a large excess of hydrogen peroxide and then potassium hydroxide is added, a precipitate is formed which dissolves in a great excess of the alkali, forming a yellow solution. This solution remains clear for a long time, but eventually a bright yellow precipitate of $Ti(OH)_4$ is formed.*

An insoluble titanium compound on being fused with sodium peroxide in a nickel crucible yields a melt which permits the extraction of all the titanium by water.† If the solution is made strongly acid with sulfuric acid, the orange-red color of pertitanic acid is apparent. If iron was present in the original insoluble titanium mineral, it is left insoluble in water after the fusion with sodium peroxide.

10. **Zinc** or **Tin** produces in acid solutions, preferably hydrochloric acid, a violet color caused by the formation of $TiCl_3$:

$$2\,TiCl_4 + \mathbf{Zn} = ZnCl_2 + 2\,TiCl_3.$$

The quadrivalent titanium compounds are *not* reduced by hydrogen sulfide or sulfurous acid.

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* A. Classen, *Ber.*, **21** (1888).

† J. H. Walton, Jr., *J. Am. Chem. Soc.* (**1907**).

11. **The Fluoride** is quantitatively changed to the dioxide by evaporation with sulfuric acid (difference from silicic acid).

$$TiF_4 + 2\,H_2SO_4 = 4\,HF\uparrow + 2\,SO_3\uparrow + \mathbf{TiO_2}.$$

12. **Ether** does not dissolve titanium chloride. By shaking the hydrochloric acid solution with ether, therefore, it is possible to separate ferric chloride from titanium chloride.

13. **Cupferron** (cf. p. 160) precipitates the yellow titanium salt of phenylnitrosohydroxylamine from acid solutions:

$$Ti^{++++} + 4\,C_6H_5NO\cdot NO^- \rightarrow \mathbf{Ti(C_6H_5NO\cdot NO)_4}.$$

In the presence of tartaric acid, iron can be removed by ammonia and ammonium sulfide and the titanium precipitated in the acidified filtrate with cupferron.

14. **Hydrosulfurous Acid,** $H_2S_2O_4$, which can be obtained by the action of zinc on sulfurous acid, or the sodium salt, $Na_2S_2O_4$, gives a violet or reddish color with dilute solutions of titanium; the color is not taken up by shaking with ether. According to Brunck,* the following reaction takes place from left to right in acid solutions and from right to left in alkaline solutions.

$$2\,TiCl_4 + Na_2S_2O_4 \rightleftarrows 2\,TiCl_3 + 2\,NaCl + 2\,SO_2.$$

Reactions in the Dry Way

Titanium compounds do not color the borax or sodium metaphosphate bead in the oxidizing flame; after continued heating in the reducing flame the bead becomes yellow while hot and violet when cold. By the addition of a little tin the violet color appears much more quickly. The addition of iron causes a brownish to red bead.

On fusing titanic acid with sodium carbonate, sodium metatitanate is formed, which is readily soluble in acids. By treatment with *hot* water, sodium metatitanate is decomposed, forming metatitanic acid, which is difficultly soluble in dilute acids. Even in cold water, sodium titanate is hydrolyzed and does not dissolve.

MANGANESE, Mn. At. Wt. 54.93

Sp. Gr. = about 8.0. M. Pt. = 1225° C.

Occurrence. — The most important manganese minerals are pyrolusite, MnO_2, orthorhombic; polianite, also MnO_2, tetragonal, isomorphous with rutile and tinstone; braunite, Mn_2O_3, tetragonal; manganite, $HMnO_2$, orthorhombic, isomorphous with göthite and diaspore; hausmannite, Mn_3O_4, tetragonal; and rhodochrosite, $MnCO_3$. Man-

* *Ann. d. Chem.*, **346**, 283. Cf. R. FRESENIUS, *Z. anal. Chem.*, **24**, 410.

ganese is a constant companion of iron, so that we find it in varying amounts in almost all iron ores.

It is a grayish-white metal which is readily oxidized in moist air, and is attacked by dilute acids, even acetic acid. It forms the following oxides:

$$MnO,\ Mn_2O_3,\ Mn_3O_4,\ MnO_2,\ (MnO_3),\ Mn_2O_7.$$

By treating any one of these oxides, except MnO, with cold, dilute hydrochloric acid a dark, greenish-brown solution is obtained, which on being heated evolves chlorine and becomes colorless. The solution then contains a bivalent manganese salt, — a derivative of MnO.

$$MnO + 2\,HCl = H_2O + MnCl_2,$$
$$Mn_2O_3 + 6\,HCl = 3\,H_2O + 2\,MnCl_2 + Cl_2\uparrow,$$
$$Mn_3O_4 + 8\,HCl = 4\,H_2O + 3\,MnCl_2 + Cl_2\uparrow,$$
$$MnO_2 + 4\,HCl = 2\,H_2O + MnCl_2 + Cl_2\uparrow,$$
$$Mn_2O_7 + 14\,HCl = 7\,H_2O + 2\,MnCl_2 + 5\,Cl_2\uparrow.$$

All manganese oxides dissolve on warming with concentrated sulfuric acid, forming manganous sulfate, accompanied (with the exception of MnO) by evolution of oxygen:

$$MnO + H_2SO_4 = H_2O + MnSO_4,$$
$$2\,Mn_2O_3 + 4\,H_2SO_4 = 4\,H_2O + 4\,MnSO_4 + O_2\uparrow,$$
$$2\,Mn_3O_4 + 6\,H_2SO_4 = 6\,H_2O + 6\,MnSO_4 + O_2\uparrow,$$
$$2\,MnO_2 + 2\,H_2SO_4 = 2\,H_2O + 2\,MnSO_4 + O_2\uparrow.$$

The behavior of the higher oxides, MnO_2, Mn_2O_3, and Mn_3O_4, with boiling dilute nitric or sulfuric acid is very interesting: MnO_2 is not attacked at all by these dilute acids; while Mn_2O_3 gives up half of its manganese to the acid, the other half remaining undissolved as brown hydrated manganese dioxide, H_2MnO_3; two-thirds of Mn_3O_4 is dissolved by these acids, brown hydrated manganese dioxide being left behind, as before.

This H_2MnO_3 separates out just as metasilicic acid is deposited from a silicate on the addition of a strong acid:

$$CaSiO_3 + 2\,H^+ \rightarrow H_2SiO_3 + Ca^{++}.$$

In fact, hydrated manganese dioxide behaves in most cases exactly like an acid, the oxides Mn_2O_3 and Mn_3O_4 behave like manganous salts of this acid and are to be regarded as manganites.

Mn_2O_3, therefore, is to be regarded as manganous manganite, $Mn\begin{smallmatrix}/O\backslash\\\backslash O/\end{smallmatrix}MnO$, of analogous composition to manganous carbonate, $MnCO_3$, and manganous metasilicate, $MnSiO_3$.

According to this conception, electrolytic dissociation should give rise to Mn^{++} cations and MnO_3^{--} anions; it is easy to understand, therefore, why Mn_2O_3 gives up half of its manganese on treatment with dilute nitric acid, with the separation of manganous acid:

$$MnMnO_3 + 2\,HNO_3 \rightleftarrows Mn(NO_3)_2 + \mathbf{H_2MnO_3}.$$

Mn_3O_4, which gives up two-thirds of its manganese, may be considered to be the manganous salt of orthomanganous acid, H_4MnO_4.

On treating $Mn_2 \cdot MnO_4$ with nitric acid, the ortho acid first separates out; it loses water, and goes over into metamanganous acid:

$$Mn_2MnO_4 + 4\,HNO_3 = 2\,Mn(NO_3)_2 + H_4MnO_4,$$

$$H_4MnO_4 = H_2O + \mathbf{H_2MnO_3}.$$

MnO_2 stands in the same relation to H_2MnO_3 as CO_2 to H_2CO_3, as SiO_2 to H_2SiO_3, and as SnO_2 to H_2SnO_3; MnO_2, therefore, behaves like an acid anhydride.

Like SnO_2 (which see), manganese dioxide behaves partly as an acid anhydride and partly as the anhydride of a base. It probably forms the chloride $MnCl_4$, for if MnO_2 is treated with cold concentrated hydrochloric acid it dissolves with a brownish-green color, forming manganese tetrachloride, soluble in ether with a green color. If, therefore, the aqueous solution of $MnCl_4$ is shaken with ether, the upper layer is colored green.

$Mn(SO_4)_2$ and $Mn_2(SO_4)_3$ are also known. These salts are hydrolyzed readily, forming H_2MnO_3 and $MnMnO_3$:

$$Mn(SO_4)_2 + 3\,H_2O \rightleftarrows \mathbf{H_2MnO_3} + 2\,H_2SO_4,$$

$$Mn_2(SO_4)_3 + 3\,H_2O \rightleftarrows \mathbf{Mn_2O_3} + 3\,H_2SO_4.$$

Not only manganous manganites, but quite a number of other manganites are known. Some of these play a very important part in analytical chemistry; for example, zinc and calcium bimanganites $ZnH_2(MnO_3)_2$, $CaH_2(MnO_3)_2$, which are analogous to calcium bicarbonate, $CaH_2(CO_3)_2$.

Zinc bimanganite is formed in the volumetric determination of manganese (see Vol. II). Calcium bimanganite is of importance technically. Thus the recovery of manganese, by the Weldon process in the manufacture of chlorine, depends upon the formation of calcium bimanganite.

Manganous oxide, MnO, is the only oxide of manganese which in all cases acts as the anhydride of a base. By dissolving this oxide in acids, manganous salts are always obtained, in which the manganese is bivalent. The oxide MnO_3 has never been isolated, but there are salts (R_2MnO_4, see p. 178) known which are derived from it. Mn_2O_7

is a distinct acid anhydride, from which the permanganates ($RMnO_4$) are derived.

In the study of the reactions of manganese, the manganous compounds will be discussed first, then the manganates and permanganates.

A. Manganous Compounds

The manganous compounds are pink both in the crystalline state and in aqueous solution; but in the anhydrous state they are colorless with the exception of the sulphide.

Reactions in the Wet Way

1. **Potassium** or **Sodium Hydroxide** precipitates white manganous hydroxide,

$$Mn^{++} + 2\,OH^- \rightarrow \mathbf{Mn(OH)_2},$$

which rapidly becomes brown in the air, owing to the formation of manganous manganites, which are less soluble than $Mn(OH)_2$.

First a part of the manganous hydroxide is oxidized by the air to manganous acid:

$$2\,\mathbf{Mn(OH)_2} + O_2 \rightleftarrows 2\,\mathbf{H_2MnO_3},$$

which, on coming in contact with the basic manganous hydroxide, immediately forms a salt with it — a manganite,

$$\mathbf{H_2MnO_3} + \mathbf{Mn(OH)_2} \rightleftarrows \mathbf{MnMnO_3} + 2\,H_2O$$

or possibly,

$$2\,\mathbf{H_2MnO_3} + \mathbf{Mn(OH)_2} \rightleftarrows \mathbf{MnH_2(MnO_3)_2} + 2\,H_2O.$$

This oxidation takes place in the air only gradually, but immediately in the presence of chlorine, bromine, hypochlorites, hydrogen peroxide, etc.:

$$\mathbf{Mn(OH)_2} + 2\,NaOH + Cl_2 = 2\,NaCl + H_2O + \mathbf{H_2MnO_3},$$

$$\mathbf{Mn(OH)_2} + H_2O_2 = H_2O + \mathbf{H_2MnO_3}.$$

Precipitated manganous acid dissolves in potassium acid oxalate solution forming a beautiful red solution of a complex mangano-oxalate ion.

The formation of manganites is of technical importance, as mentioned on p. 171. The residue obtained in the preparation of chlorine from pyrolusite and hydrochloric acid consists chiefly of manganese chloride; by adding lime to it, manganous hydroxide is formed. This mixture of manganous hydroxide and lime is exposed to the action of the atmosphere, whereby manganous acid is formed, which unites with the calcium as the stronger base, forming calcium bimanganite, so that finally all of the manganese is oxidized to manganous acid:

$$2\,\mathbf{Mn(OH)_2} + O_2 + Ca(OH)_2 = 2\,H_2O + \mathbf{CaH_2(MnO_3)_2}.$$

On treating the residue, when in the right condition, with hydrochloric acid again, the same amount of chlorine is obtained as from the original pyrolusite:

$$2\,\mathbf{MnO_2} + 8\,HCl = 4\,H_2O + 2\,MnCl_2 + 2\,Cl_2\uparrow.$$

$$\mathbf{CaH_2(MnO_3)_2} + 10\,HCl = 6\,H_2O + 2\,MnCl_2 + CaCl_2 + 2\,Cl_2\uparrow.$$

It is, however, necessary to add a little more hydrochloric acid in the latter case, because a part of the acid is used up in setting the manganous acid free from the manganite.

2. **Ammonia** precipitates from neutral solutions free from ammonium salts (as with magnesium and ferrous salts) a part of the manganese as the white hydroxide:

$$MnCl_2 + NH_4OH \rightleftarrows \mathbf{Mn(OH)_2} + 2\,NH_4Cl.$$

If sufficient ammonium chloride is present, ammonia causes no precipitation (cf. p. 98). The greater part of the manganese then remains in solution as manganous chloride, but a small amount exists as the hydroxide. On standing in the air, this dissolved hydroxide is changed slowly into the more difficultly soluble manganous acid, which is deposited in brown flocks. The condition of equilibrium in the solution is thereby disturbed, and in order to restore it more hydroxide is formed, and the reaction continues in this way until finally all of the manganese may be precipitated. This fact must be considered in the separation of manganese from ferric iron, aluminium, etc. If a solution of ferric and manganous chlorides contains sufficient ammonium chloride, none of the manganese and all of the iron will be precipitated on the addition of ammonia, but, if the solution stands in contact with the air, gradually the manganese will be precipitated. In effecting the separation, therefore, an excess of ammonium chloride should be present, the solution boiled to remove the air as much as possible from the solution, then a *slight* excess of ammonia should be added and the solution filtered *immediately*. The separation even then is not quantitative, but is satisfactory for qualitative analysis.

Oxidizing agents in the presence of ammonia cause the precipitation of manganese as H_2MnO_3. Bromine is ordinarily used as the oxidizing agent, but a number of precautions are necessary to accomplish the complete precipitation of manganese by means of bromine and ammonia.

If a neutral solution of manganous salt is treated with bromine, the precipitation of manganese as H_2MnO_3 is always incomplete:

$$Mn^{++} + Br_2 + 3\,H_2O \rightleftarrows 4\,H^+ + 2\,Br^- + \mathbf{H_2MnO_3}.$$

The precipitation of the manganese can be made complete, in accordance with the mass-action principle (p. 13), if the hydrogen ions formed in the reaction are neutralized; sodium bromide in neutral solution will not reduce H_2MnO_3, but hydrobromic acid will do so. The solution may be neutralized by caustic alkali, alkali carbonate, alkali acetate (cf. p. 46), or ammonia. A solution of manganous

salt may contain a considerable excess of acetic acid and yet the manganese will be completely precipitated by bromine in the presence of sodium acetate.

Ammonia is not altogether satisfactory as a neutralizing agent in this case because it reacts with bromine as well as with hydrobromic acid. When bromine is added to ammonia solution, a vigorous reaction takes place and nitrogen is evolved (cf. p. 96):

$$8\,NH_4OH + 3\,Br_2 = 6\,NH_4Br + 8\,H_2O + N_2\uparrow.$$

When bromine is added to a solution of ammonium chloride a very slow oxidation results and nitrogen gas is evolved:

$$2\,NH_4^+ + 3\,Br_2 \rightleftarrows 8\,H^+ + 6\,Br^- + N_2\uparrow.$$

If sodium acetate is added to this solution, the reaction is accelerated greatly as a result of diminishing the concentration of the hydrogen ions, and by heating the solution, which increases the speed of the reaction and causes the rapid expulsion of nitrogen gas, all of the ammonium salt can be decomposed by means of a very slight excess of bromine.

The presence of ammonium salts prevents the precipitation of manganese by bromine and sodium acetate; when all the ammonium salt has been oxidized to nitrogen, the manganese can be precipitated as H_2MnO_3 provided the solution is not allowed to become acid.

The conditions are more favorable for the precipitation of manganese when the solution contains hydroxyl ions, as in an ammoniacal solution. The addition of bromine to such a solution usually results in the immediate precipitation of some of the manganese but, as a result of the action of bromine on ammonia or ammonium salt, the solution usually becomes acid and the precipitation of the manganese is then incomplete. To precipitate all of the manganese by means of ammonia and bromine, it is best to proceed as follows:

Dilute the solution to about 200 cc. and neutralize, if necessary, with ammonia. Add a little bromine water, a slight excess of ammonia and stir to promote the formation of a precipitate. Heat the solution, add a little more bromine water and make slightly ammoniacal again. In case the amount of the manganese precipitate is perceptibly increased by this last treatment with bromine and ammonia, repeat the operation. Filter off the precipitated H_2MnO_3, concentrate the solution somewhat by evaporation and again treat with bromine water and ammonia. Sometimes H_2MnO_3 is precipitated on the sides of the vessel during evaporation. The treatment with bromine and ammonia should be continued until a filtrate is obtained which will not give any more precipitate with these reagents.*

3. **Alkali Carbonates** precipitate white manganous carbonate,

$$Mn^{++} + CO_3^{--} \rightarrow \mathbf{MnCO_3},$$

which after long boiling is changed by the oxygen of the air into less soluble, hydrated manganese dioxide:

$$2\,MnCO_3 + 2\,H_2O + O_2 = 2\,CO_2\uparrow + \mathbf{2\,H_2MnO_3}.$$

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* The above explanation is given at length because of its importance in quantitative analysis. The facts upon which the explanation is based have been carefully verified by quantitative experiments performed by S. G. Simpson in the laboratory of the translator.

4. **Ammonium Carbonate** precipitates the white carbonate even in the presence of ammonium salts (difference from magnesium).

5. **Barium Carbonate** produces a precipitate only in hot solutions.

6. **Sodium Phosphate** precipitates white, tertiary manganous phosphate,

$$4\,HPO_4^{--} + 3\,Mn^{++} \rightarrow 2\,H_2PO_4^- + \mathbf{Mn_3(PO_4)_2},$$

soluble in mineral acids and in acetic acid:

$$\mathbf{Mn_3(PO_4)_2} + 2\,H^+ \rightleftarrows 3\,Mn^{++} + 2\,HPO_4^{--}.$$

If to the boiling solution of this precipitate in acid an excess of ammonia is added, manganous ammonium phosphate will be precipitated, as with magnesium (see p. 99):

$$HPO_4^{--} + NH_4OH \rightleftarrows NH_4^+ + PO_4^{---} + H_2O.$$

$$Mn^{++} + NH_4^+ + PO_4^{---} + 7\,H_2O \rightarrow \mathbf{Mn(NH_4)PO_4 \cdot 7\,H_2O}.$$

The crystalline precipitate is flesh colored and is practically insoluble in water.

7. **Lead Peroxide and Concentrated Nitric Acid.** (Volhard's reaction). — If a solution containing only traces of manganese is boiled with lead peroxide and concentrated nitric acid, then diluted with water and the residue allowed to settle, the supernatant liquid acquires a distinct violet-red color, owing to the formation of permanganic acid:

$$2\,Mn^{++} + 5\,\mathbf{PbO_2} + 4\,H^+ \rightarrow 5\,Pb^{++} + 2\,H_2O + 2\,MnO_4^-.$$

This extremely delicate reaction does not take place in the presence of much hydrochloric acid or chlorides, because the permanganic acid is thereby destroyed:

$$2\,HMnO_4 + 14\,HCl = 8\,H_2O + 2\,MnCl_2 + 5\,Cl_2\uparrow.$$

8. **Sodium Bismuthate** added to a cold solution of a manganous salt in dilute nitric acid (about sp. gr. 1.13) causes the formation of permanganic acid. The reagent, which corresponds approximately to the symbol $NaBiO_3$, is prepared by fusing bismuth oxide with sodium peroxide; it is insoluble in water and the excess of reagent may be filtered off through asbestos after applying the test. The reaction may be expressed by the equation:

$$2\,Mn^{++} + 5\,NaBiO_3 + 16\,H^+ \rightarrow 5\,Na^+ + 5\,Bi^{+++} + 7\,H_2O + 2\,HMnO_4.$$

The test is extremely delicate when nothing is present that will react with the permanganate formed. An insoluble carbonaceous residue, such as remains after the solution of cast iron in acid, must be filtered off before adding the reagent. If the solution is heated, the

permanganic acid breaks down and hydrated manganese dioxide is precipitated.

Bismuth dioxide, BiO_2, may be used instead of sodium bismuthate.

9. **Ammonium Persulfate.**—If a hot solution of a manganous salt in either dilute sulfuric or nitric acid is treated with ammonium persulfate, all the manganese is gradually oxidized to the quadrivalent condition and a precipitate of hydrated manganese dioxide is formed:

$$Mn^{++} + S_2O_8^{--} + 3\,H_2O \rightarrow 2\,SO_4^{--} + 4\,H^+ + \mathbf{H_2MnO_3}.$$

If, however, the solution contains a trace of silver nitrate as catalyzer, then the oxidation goes farther and permanganic acid is formed:

$$2\,Mn^{++} + 5\,S_2O_8^{--} + 8\,H_2O \rightarrow 16\,H^+ + 10\,SO_4^{--} + 2\,MnO_4^-.$$

This reaction is quantitative for small amounts of manganese and in the absence of anything that will react with the permanganic acid.*

10. **Ammonium Sulfide** precipitates from manganese solutions flesh-colored, hydrated manganese sulfide:

$$Mn^{++} + S^{--} \rightarrow \mathbf{MnS}.$$

On boiling with a large excess of ammonium sulfide it is changed into less hydrated *green* manganese sulfide of the formula, $3\,MnS + H_2O$.

The solubility product of MnS is relatively large (cf. p. 22) and to precipitate all the manganese as sulfide an excess of S^{--} ions is necessary. The precipitate dissolves readily in dilute acid as a result of the removal of the S^{--} ions to form non-ionized hydrogen sulfide (cf. p. 48).

11. **Potassium Cyanide.** — On adding potassium cyanide to a solution of a manganous salt, a brown precipitate appears which dissolves in an excess of potassium cyanide, forming a brown solution. On standing, or by heating the solution, a voluminous green precipitate of $K[Mn(CN)_3]$ is formed which is soluble in strong potassium cyanide solution:

$$Mn^{++} + 2\,CN^- \rightleftarrows \mathbf{Mn(CN)_2},\ \mathbf{Mn(CN)_2} + KCN \rightleftarrows \mathbf{K[Mn(CN)_3]}$$
$$\mathbf{K[Mn(CN)_3]} + 3\,CN^- \rightleftarrows K^+ + [Mn(CN)_6]^{---}.$$

To keep the manganese in solution in the form of $Mn(CN)_6^{---}$ ions, it is necessary to use an excess of potassium cyanide. If the concentration of the cyanide is diminished by dilution, some green $K[Mn(CN)_3]$ is formed and if the dilute cyanide solution is boiled, a precipitate of $Mn(OH)_2$ results:

$$[Mn(CN)_6]^{---} + 2\,H_2O \rightleftarrows 2\,HCN + 4\,CN^- + \mathbf{Mn(OH)_2}.$$

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* Cf. M. MARSHALL, *Z. anal. Chem.*, **43**, 418, 655 (1904).

The stability of these complex cyanides, therefore, is much less than that of the corresponding nickel compounds (p. 184). This permits an interesting method of separating nickel from manganese.

Nickel sulfide is much less soluble than manganous sulfide (cf. p. 22) so that it is possible to precipitate nickel as sulfide in the presence of acetic acid and sodium acetate; under these conditions no manganese sulfide is formed. If, on the other hand, ammonium sulfide is added to a hot, dilute solution containing the complex cyanides of nickel and manganese, the nickel will remain in solution and the precipitation of the manganese as sulfide will be complete:

$$[Mn(CN)_6]^{--} + S^{--} \rightleftarrows 6\,CN^- + \mathbf{MnS}.$$

In the presence of a large excess of potassium cyanide, however, the $[Mn(CN)_6]^{--}$ anion is so stable that none of the manganese is precipitated in the cold by ammonium sulfide.

12. **Potassium Chlorate.** — By boiling a solution of manganous salt in concentrated nitric acid with an excess of potassium chlorate, all of the manganese is precipitated as MnO_2.

$$Mn(NO_3)_2 + 2\,KClO_3 \rightarrow \mathbf{MnO_2} + 2\,KNO_3 + 2\,ClO_2\uparrow.$$

13. **Potassium Ferrocyanide** precipitates white manganous ferrocyanide, $Mn_2[Fe(CN)_6]$, which is difficultly soluble in hydrochloric acid. The precipitate can be obtained also in a solution which has been treated with tartaric acid and ammonia.

14. **Potassium Ferricyanide** forms brown manganous ferricyanide, $Mn_3[Fe(CN)_6]_2$, slightly soluble in cold hydrochloric acid and insoluble in ammonia.

15. **Potassium Bromate** added to a cold sulfuric acid solution of a manganous salt gives the violet color of permanganate. The chlorate and iodate do not give the reaction.

16. **Potassium Periodate** gives a deep red precipitate, or a red color with dilute solutions, of manganous periodate, presumably. Hydrochloric acid dissolves the precipitate with evolution of chlorine; caustic soda and even ammonia, changes it into black manganous acid, H_2MnO_3. The reaction is delicate and is aided by heating.

17. **Oxidizing Agents** added to a saturated solution of manganous chloride in concentrated hydrochloric acid give, on heating, a deep brown or black coloration due to the formation of manganese tetrachloride. The reaction is given by a nitrate, chlorate, hypochlorite, or chromate and by lead peroxide. It fails with perchlorate, bromate, bromine, sodium peroxide, persulfate, nitrite and red lead.*

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* DE KONINCK, *Z. anal. Chem.*, **43**, 418.

Reactions in the Dry Way

The borax, or salt of phosphorus bead, is amethyst red after heating in the oxidizing flame with small amounts of manganese, almost brown with larger amounts, and can then be mistaken for the nickel bead. Heated in the reducing flame, the manganese bead becomes colorless, while the nickel bead appears gray.

On fusing any manganous compound with caustic alkali or alkali carbonate (on platinum foil) in the air, or, better still, in the presence of an oxidizing agent (such as potassium nitrate, potassium chlorate, etc.), a green melt is obtained, owing to the formation of the alkali salt of manganic acid, as is shown by the following equations:

$$MnO + Na_2CO_3 + O_2 = CO_2\uparrow + Na_2MnO_4,$$
$$2\,MnO_2 + 2\,Na_2CO_3 + O_2 = 2\,CO_2\uparrow + 2\,Na_2MnO_4,$$
$$2\,Mn_2O_3 + 4\,Na_2CO_3 + 3\,O_2 = 4\,CO_2\uparrow + 4\,Na_2MnO_4,$$
$$2\,Mn_3O_4 + 6\,Na_2CO_3 + 5\,O_2 = 6\,CO_2\uparrow + 6\,Na_2MnO_4,$$
$$MnSO_4 + 2\,Na_2CO_3 + O_2 = 2\,CO_2\uparrow + Na_2SO_4 + Na_2MnO_4.$$

The oxygen comes either from the air or from the nitrate or chlorate:

$$2\,KNO_3 = 2\,KNO_2 + O_2, \quad 2\,KClO_3 = 2\,KCl + 3\,O_2\uparrow.$$

This reaction is exceedingly delicate; a fraction of a milligram of any manganese compound can be recognized by the formation of this green color.

By ignition in the air the oxides of manganese are changed to Mn_3O_4:

$$6\,MnO + O_2 = 2\,Mn_3O_4, \quad 3\,MnO_2 = Mn_3O_4 + O_2\uparrow,$$
$$6\,Mn_2O_3 = 4\,Mn_3O_4 + O_2\uparrow.$$

B. Manganic and Permanganic Acids

Free manganic acid has never been isolated. If we attempt to form it from the green melt of the alkali manganate by the addition of acid, permanganic acid and hydrated manganese dioxide will be obtained; a part of the unstable manganic acid oxidizes another part of the same to permanganic acid, while the oxidizing part is itself reduced to hydrated manganese dioxide:

$$3\,H_2MnO_4 = 2\,HMnO_4 + \mathbf{H_2MnO_3} + H_2O.$$

This transformation takes place so readily that the green solution of the manganate is changed to a reddish-violet solution of a permanganate by simply standing in the air, with the help of the carbonic acid which the air always contains:

$$3\,K_2MnO_4 + 2\,CO_2 + H_2O = 2\,K_2CO_3 + \mathbf{H_2MnO_3} + 2\,KMnO_4.$$

The reaction takes place much more rapidly, however, if a few drops of a strong acid are added.

The oxidation of one molecule at the expense of another of the same kind is of quite common occurrence in chemistry. It always involves a loss in the *available* or *free energy* which the molecules originally possessed. The total energy possessed by any molecule can be considered to consist partly of free energy and partly of unavailable energy. A reaction that takes place spontaneously is always characterized by the fact that the free energy of the system is less afterward than it was before the reaction took place. The condition with the smallest free energy is the most stable condition.

It might be inferred that the most stable conditions are those having the smallest quantities of energy, but a little consideration shows that in promoting chemical reactions it is not so much the total energy as it is the available energy which comes into consideration. Thus, there is a vast amount of energy stored up in the heat of the ocean, but it is not available energy, because it is in surroundings at the same temperature. The air under ordinary atmospheric pressure could perform a great deal of work if it were brought in contact with a space in which a much lower gas-pressure prevailed, but otherwise the vast amount of energy is not available.

In the changes that take place with any given element it is not necessarily true that an increase in the total energy will always involve an increase in the free energy associated with the element. The fact that the solution of a manganate, in which the valence of the manganese is six, decomposes readily indicates merely that the free energy in the system composed of quadrivalent and heptavalent manganese is less than the free energy involved in the system containing all the manganese in the hexavalent condition. Frequently the conditions are just the reverse and the most stable condition is one of intermediate valence. Thus permanganate and manganous salt react to form quadrivalent manganese. A few reactions similar to the decomposition of H_2MnO_4 will be given.

Hypochlorites are changed, by warming the aqueous solution, into chlorate and chloride; one atom of chlorine is oxidized from the valence of one to the valence of five at the expense of two atoms of chlorine, which are reduced from a positive valence of one to a negative valence of one:

$$3\,NaClO = NaClO_3 + 2\,NaCl.$$

Ignition of a chlorate causes the formation of a perchlorate, a chloride and free oxygen. Here one atom of chlorine is increased two in valence, one atom of chlorine loses six charges and the remaining four charges cause the oxidation of two atoms of negatively charged oxygen:

$$2\,NaClO_3 = NaClO_4 + NaCl + O_2\uparrow.$$

Nitrous acid is changed in aqueous solution into nitric acid and nitric oxide, one atom of nitrogen gaining two charges and two similar atoms losing one charge:

$$3\,HNO_2 = HNO_3 + 2\,NO\uparrow + H_2O.$$

Hypophosphorous acid and also phosphorous acid can be changed into phosphoric acid and phosphine:

$$2\,H_3PO_2 = H_3PO_4 + PH_3\uparrow,\quad 4\,H_3PO_3 = 3\,H_3PO_4 + PH_3\uparrow.$$

Alkali thiosulfates and alkali sulfites are changed by ignition into sulfate and sulfide:

$$4\,Na_2S_2O_3 = 3\,Na_2SO_4 + Na_2S_5,\quad 4\,Na_2SO_3 = 3\,Na_2SO_4 + Na_2S.$$

Permanganic Acid, $HMnO_4$, although much more stable than manganic acid, is known only in aqueous solution; but the anhydride Mn_2O_7 has been isolated. On cautiously adding concentrated sulfuric acid to the cooled solution of a permanganate, oily drops of reddish-brown Mn_2O_7 separate out, which, however, on being warmed (the heat of reaction is sufficient), explode with scintillation:

$$2\,Mn_2O_7 + 4\,H_2SO_4 = 4\,MnSO_4 + 4\,H_2O + 5\,O_2\uparrow.$$

The salts of permanganic acid (the permanganates) are all soluble in water, with a reddish-violet color, and are very energetic oxidizing agents. In acid solution the heptavalent manganese in permanganate is usually reduced to bivalent manganous salt, but in alkaline, or nearly neutral, solutions manganese dioxide is the usual product.

Oxidation in Acid Solution. — Typical oxidation equations with permanganate have already been explained on p. 31. A few of these reactions will be repeated here, but it will not be necessary to enter into further details concerning the method of balancing the equations. To avoid exact repetition, the equations will be given with the entire molecules written instead of merely the ions involved,

$$2\,KMnO_4 + 3\,H_2SO_4 + 10\,HCl = K_2SO_4 + 2\,MnSO_4 + 8\,H_2O + 5\,Cl_2\uparrow,$$
$$2\,KMnO_4 + 3\,H_2SO_4 + 10\,HI = K_2SO_4 + 2\,MnSO_4 + 8\,H_2O + 5\,I_2,$$
$$2\,KMnO_4 + 3\,H_2SO_4 + 5\,H_2S = K_2SO_4 + 2\,MnSO_4 + 8\,H_2O + 5\,\mathbf{S},$$
$$8\,KMnO_4 + 12\,H_2SO_4 + 5\,PH_3 = 4\,K_2SO_4 + 8\,MnSO_4 + 12\,H_2O + 5\,H_3PO_4,$$
$$2\,KMnO_4 + 6\,SO_2 + 2\,H_2O = 2\,KHSO_4 + 2\,MnSO_4 + H_2S_2O_6.$$

In this last equation the proportion of sulfate and of dithionic acid, $H_2S_2O_6$, will vary with the temperature and concentration of the solution:

$$2\,KMnO_4 + 5\,H_2C_2O_4 + 3\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 8\,H_2O + 10\,CO_2\uparrow,$$
$$2\,KMnO_4 + 5\,H_2O_2 + 4\,H_2SO_4 = 2\,KHSO_4 + 2\,MnSO_4 + 8\,H_2O + 5\,O_2\uparrow,$$
$$2\,KMnO_4 + 5\,K_2C_2O_6 + 14\,H_2SO_4$$
$$= 12\,KHSO_4 + 2\,MnSO_4 + 8\,H_2O + 10\,CO_2\uparrow + 5\,O_2\uparrow.$$

Persulfuric acid, which is analogous to percarbonic acid, does not reduce a solution of a permanganate. An interesting reaction is that which takes place in nearly neutral solution between permanganate and manganous ions. The principal product is MnO_2, which will carry down some of the bivalent manganese as manganous manganite unless an excess of some other ion is present which forms an insoluble manganite, e.g., zinc or calcium ions:

$$2\,KMnO_4 + 3\,MnSO_4 + 2\,H_2O = 2\,KHSO_4 + 5\,\mathbf{MnO_2} + H_2SO_4.$$

Oxidation in Alkaline Solution. — Many *organic* substances are oxidized by permanganates in alkaline solution with precipitation of manganese dioxide. Thus formic acid is oxidized to carbonic acid, ethyl alcohol to aldehyde and acetic acid, cellulose (paper) chiefly to oxalic acid, so that a solution of a permanganate cannot be filtered through paper. By boiling a concentrated solution of potassium permanganate with concentrated potassium hydroxide, potassium manganate is formed with evolution of oxygen, and the color of the solution becomes green:

$$4\,KMnO_4 + 4\,KOH = 4\,K_2MnO_4 + 2\,H_2O + O_2\uparrow.$$

By heating solid potassium permanganate to 240° C., potassium manganate is formed, also with evolution of oxygen:

$$2\,KMnO_4 = K_2MnO_4 + MnO_2 + O_2\uparrow.$$

NICKEL, Ni. At. Wt. 58.68

Sp. Gr. = 8.9. M. Pt. = 1452° C.

Occurrence. — In the native state nickel occurs only in meteorites. It is most frequently found in combination with sulfur, arsenic, and antimony in regular and hexagonal crystallizing minerals, of which the following are the most important:

Isometric System: Chloanthite, $NiAs_2$; gersdorffite, NiAsS; ullmannite, NiSbS. *Hexagonal System:* Niccolite, Ni_2As_2; breithauptite, Ni_2Sb_2; millerite, Ni_2S_2.

Nickel also occurs as regular crystals of bunsenite, NiO, isomorphous with periclasite, MgO, and manganosite, MnO; as garnierite or noumeite, $H_2(NiMg)SiO_4$ + aq, a mineral occurring in New Caledonia, from which pure nickel can be prepared; and finally as annabergite, $Ni_3(AsO_4)_2 \cdot 8\,H_2O$, isomorphous with erythrite.

Metallic nickel possesses a silver-white color and is difficultly soluble in hydrochloric and sulfuric acids, but readily soluble in nitric acid. It forms two oxides: green nickelous oxide, NiO, and brownish black nickelic oxide, Ni_2O_3.

By dissolving either of these oxides in acids, salts of bivalent nickel are always obtained:

$$NiO + 2\,HCl = H_2O + NiCl_2,$$

$$Ni_2O_3 + 6\,HCl = 3\,H_2O + 2\,NiCl_2 + Cl_2\uparrow,$$

$$2\,Ni_2O_3 + 4\,H_2SO_4 = 4\,H_2O + 4\,NiSO_4 + O_2\uparrow.$$

Nickelous oxide behaves as a basic anhydride, but nickelic oxide acts as a peroxide and forms no salts.

The crystallized salts of nickel and their aqueous solutions are

green, but in the anhydrous condition they are usually yellow. Most of the salts are soluble in water; the sulfide, carbonate, and phosphate are insoluble.

Reactions in the Wet Way

1. **Potassium Hydroxide** precipitates apple-green nickelous hydroxide,

$$Ni^{++} + 2\,OH^- \rightarrow \mathbf{Ni(OH)_2},$$

insoluble in excess of the precipitant, readily soluble in acids.

Boiling the solution and adding hydrogen peroxide or iodine does not serve to oxidize the nickelous hydroxide but bromine water, sodium hypochlorite, potassium ferricyanide or a persulfate changes it to black nickelic hydroxide.

The presence of non-volatile organic acids and sugar prevents the precipitation of the bivalent and trivalent nickel.

Nickelous hydroxide dissolves in ammonium carbonate solution giving a greenish blue liquid and in potassium cyanide to form potassium nickelo-cyanide. It also dissolves slowly in a mixture of ammonia and ammonium chloride forming nickelous-ammonia complex ions.

2. **Ammonia** precipitates (in neutral solutions free from ammonium salts) a green basic salt,

$$2\,NiSO_4 + 2\,NH_4OH = (NH_4)_2SO_4 + \mathbf{Ni_2SO_4 \cdot (OH)_2},$$

soluble (with a blue color) in excess of ammonia, forming complex nickel ammonia ions (cf. p. 25).

$$\mathbf{Ni_2SO_4 \cdot (OH)_2} + 12\,NH_3 \rightarrow 2\,[Ni(NH_3)_6]^{++} + 2\,OH^- + SO_4^{--}.$$

In the presence of sufficient ammonium salt, ammonia produces no precipitate, as with magnesium, ferrous and manganous salts; potassium and sodium hydroxides, however, precipitate the green hydroxide (difference from cobalt, see p. 189).

The anhydrous chloride and sulfate readily absorb ammonia, forming anhydrous nickel ammonium salts:

$$NiCl_2 + 6\,NH_3 = [Ni(NH_3)_6]Cl_2;\ NiSO_4 + 6\,NH_3 = [Ni(NH_3)_6]SO_4.$$

The nickel ammonia cations are very stable in the presence of an excess of ammonia. In pure water they are in equilibrium with a small quantity of nickel ions, dissolved ammonia, and ammonium hydroxide:

$$[Ni(NH_3)_6]^{++} \rightarrow Ni^{++} + 6\,NH_3;\ NH_3 + H_2O \rightarrow NH_4OH.$$

3. **Potassium** and **Sodium Carbonates** precipitate apple-green nickel carbonate:

$$Ni^{++} + CO_3^{--} \rightarrow \mathbf{NiCO_3}.$$

4. **Ammonium Carbonate** behaves similarly, but the precipitate is soluble in an excess of the precipitant, forming nickel ammonia carbonate.

5. **Sodium Hypochlorite** precipitates in the presence of alkalies all of the nickel as brownish-black nickelic hydroxide, $Ni(OH)_3$. Nickelous hydroxide is first formed by the alkali present, but it is then oxidized by the hypochlorite to nickelic hydroxide:

$$2\,Ni^{++} + 4\,OH^- + ClO^- + H_2O \rightarrow 2\,\mathbf{Ni(OH)_3} + Cl^-.$$

On adding chlorine or bromine to the nickel solution to which alkali has been added, nickelic hydroxide is likewise formed:

$$2\,\mathbf{Ni(OH)_2} + 2\,OH^- + Cl_2 \rightarrow 2\,Cl^- + 2\,\mathbf{Ni(OH)_3}.$$

6. **Barium Carbonate** produces in the cold no precipitation; but by continued boiling, all of the nickel is thrown down as basic carbonate.

7. **Hydrogen Sulfide** precipitates no nickel from solutions which contain mineral acid or much acetic acid; but from solutions slightly acid with acetic acid and containing an alkali acetate, all the nickel is precipitated as the black sulfide:

$$Ni^{++} + 2\,C_2H_3O_2^- + H_2S \rightarrow 2\,HC_2H_3O_2 + \mathbf{NiS}.$$

8. **Ammonium Sulfide** precipitates from neutral solutions the nickel as sulfide:

$$NiCl_2 + (NH_4)_2S = 2\,NH_4Cl + \mathbf{NiS}.$$

Nickel sulfide has a marked tendency to form colloidal solutions of a dark-brown color, especially in the presence of ammonia or a considerable excess of ammonium sulfide. By making the brown solution slightly acid with acetic acid and boiling, the hydrosole is coagulated and can be removed by filtration. The presence of ammonium salts also favors the coagulation of the hydrosole.

9. Villiers has developed a very sensitive test which depends upon the formation of a brown colloidal solution of nickel sulfide. The nickel salt solution is treated with tartaric acid and a slight excess of sodium hydroxide and is then saturated with hydrogen sulfide: a part of the nickel always remains in solution and colors it dark brown. Cobalt ions are precipitated as cobalt sulfide by this treatment except when only a trace of cobalt is present when it is likely to give a brown color; caustic soda, however, causes the cobalt sulfide to precipitate.

If it is desired to precipitate the nickel as sulfide from an ammoniacal solution, it is best to make the solution very slightly acid, add a little ammonium chloride unless considerable is already present, heat to boiling, add colorless ammonium

sulfide drop by drop until no further precipitation takes place, and then add 0.5 to 1 cc. of the reagent in excess. The nickel sulfide thus obtained can be filtered without difficulty and the filtrate is free from nickel. During the filtration care should be taken to keep the filter well filled with liquid to prevent the oxidation of the precipitate, which takes place readily on exposure to the air. To wash the precipitate it is well to use a hot, 5 to 10 per cent ammonium chloride solution to which a little colorless ammonium sulfide has been added. The washing can also be effected with hydrogen sulfide water without there being any danger of hydrosole formation.

Nickel sulfide is difficultly soluble in dilute mineral acids, readily soluble, however, in strong nitric acid or in aqua regia, with separation of sulfur:

$$3\,\mathbf{NiS} + 6\,HCl + 2\,HNO_3 = 3\,NiCl_2 + 2\,NO\uparrow + 4\,H_2O + 3\,\mathbf{S}.$$

The sulfur usually separates out as a black film. This is caused by the sulfur first melting, owing to the heat of reaction, enclosing small particles of the black sulfide and protecting them from the action of the acid. By continued action of the acid all the sulfide is dissolved, and the sulfur remains as yellow drops, which are oxidized little by little to sulfuric acid,

$$\mathbf{S} + 2\,HNO_3 = H_2SO_4 + 2\,NO\uparrow.$$

Nickel and cobalt sulfides, though not precipitated by hydrogen sulfide from a dilute, hydrochloric acid solution, dissolve with difficulty in a much stronger acid. This is perhaps due to the fact that these sulfides exist in two allotropic forms of different solubilities. The sulfide first precipitated is readily soluble in acid, but on standing it becomes changed into a much more insoluble condition. Most schemes of qualitative analysis are based upon this behavior; the nickel and cobalt are separated from zinc and manganese by treating the ammonium sulfide precipitate with cold, dilute hydrochloric acid. In such cases some nickel and cobalt always pass into solution and the quantity dissolved may be much larger than is ordinarily assumed. If the surface exposed to the action of the acid is large, or if left in a finely divided state by the dissolving out of other sulfide, a considerable quantity of nickel dissolves in a comparatively short time. The reverse reaction, the precipitation of nickel sulfide by hydrogen sulfide in very dilute acid solution, also takes place very slowly but continuously.*

10. **Potassium Cyanide** produces a light-green precipitate of nickelous cyanide readily soluble in an excess of the precipitant, forming potassium nickelocyanide:

$$Ni^{++} + 2\,CN^- \rightarrow \mathbf{Ni(CN)_2};$$
$$\mathbf{Ni(CN)_2} + 2\,CN^- \rightarrow [Ni(CN)_4]^{--}.$$

The $[Ni(CN)_4]^{--}$ anion is a stable complex, but it is decomposed by the addition of acid. This is because $H_2[Ni(CN)_4]$ is a very weak acid and, like carbonic acid, is unstable:

$$[Ni(CN)_4]^{--} + 2\,H^+ \rightleftarrows H_2[Ni(CN)_4];$$
$$H_2[Ni(CN)_4] \rightleftarrows 2\,HCN + \mathbf{Ni(CN)_2}.$$

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* Cf. NOYES, BRAY and SPEAR, *J. Am. Chem. Soc.*, **1908**.

In alkaline solutions, containing an excess of cyanide, the $[Ni(CN)_4]^{--}$ anion is not dissociated to a sufficient extent into simple Ni^{++} cations to give a precipitate with ammonium sulfide (difference from manganese and zinc) but it is readily decomposed by an oxidizing agent such as chlorine, bromine, hypochlorite or hypobromite

$$2\,[Ni(CN)_4]^{--} + 4\,OH^- + 9\,BrO^- + H_2O \rightarrow 2\,\mathbf{Ni(OH)_3} + 8\,CNO^- + 9\,Br^-,$$

or

$$2\,[Ni(CN)_4]^{--} + 6\,OH^- + 9\,Cl_2 \rightarrow 2\,\mathbf{Ni(OH)_3} + 8\,CNCl + 10\,Cl^-.$$

In the above reactions, first of all any excess alkali cyanide present is oxidized to cyanate or to CNCl. In the absence of an excess of cyanide ions, the $[Ni(CN)_4]^{--}$ begins to dissociate, $[Ni(CN)_4]^{--} \rightarrow Ni^{++} + 4\,CN^-$, and as fast as the ions are formed, they both become oxidized.

When cobalt ions are treated with an excess of cyanide ions a cobaltocyanide anion, $[Co(CN)_6]^{=-}$, is formed which is readily oxidized even by the oxygen of the air to form cobalticyanide ions, $[Co(CN)_6]^{---}$. These anions are so stable that they are not decomposed by treatment with oxidizing agents in alkaline solution so that no cobalt is precipitated with $Ni(OH)_3$ by the above treatment. It is possible to detect 0.2 mg. nickel in the presence of 300 mg. of cobalt by this reaction.

The test can be applied to the solution obtained by dissolving the sulfides of nickel and cobalt in aqua regia as follows: Evaporate the solution nearly to dryness to expel most of the acid, add about 5 cc. of water and then sodium hydroxide solution, drop by drop, until the solution is neutral or until a permanent precipitate is produced. Add potassium cyanide solution, a few drops at a time, until all or nearly all of any precipitated cyanide redissolves. Then add 0.5 to 3 cc. more of potassium cyanide solution according to the probable amount of nickel and cobalt present. Heat to 50° or 60° in an open dish for five minutes, or longer if the solution has not become light-colored. This serves to oxidize the cobaltocyanide to cobalticyanide. Filter off and reject any small precipitate that may remain. Add about 3 cc. of 2 N sodium hydroxide solution and conduct chlorine into the solution in the cold or add a little bromine water. A precipitate of $Ni(OH)_3$ should form within five minutes.

11. **Sodium Phosphate** precipitates apple-green nickel phosphate,

$$3\,Ni^{++} + 4\,HPO_4^{--} \rightarrow 2\,H_2PO_4^- + \mathbf{Ni_3(PO_4)_2},$$

readily soluble in acids, even acetic acid.

12. **Potassium Nitrite** produces in dilute nickel solutions no precipitate (difference from cobalt). In very concentrated solutions a brownish-red precipitate of $Ni(NO_2)_2 \cdot 4\,KNO_2$ is thrown down; in the presence of alkaline earth salts a yellow crystalline precipitate is formed; e.g., $Ni(NO_2)_2 \cdot Ba(NO_2)_2 \cdot 2\,KNO_2$, which is very difficultly soluble in cold water, but readily soluble in boiling water, with a green color.

13. **Dimethylglyoxime.** — The reagent is prepared by dissolving 1 gm. of the solid in 100 cc. of 98 per cent alcohol. If a little of the reagent is added to a solution of a nickel salt, then ammonia to slightly

alkaline reaction, and the solution is boiled, a red crystalline precipitate of the nickel salt of dimethylglyoxime is formed:

$$2\begin{matrix} CH_3 - C = NOH \\ | \\ CH_3 - C = NOH \end{matrix} + NiCl_2 + 2\,NH_3 = 2\,NH_4Cl + (C_8H_{14}N_4O_4)Ni.$$

If the quantity of nickel present is very small, at first a yellowish solution is obtained from which, on cooling, red needles are deposited. According to L. Tschugaeff,* who first proposed this qualitative test, the presence of one part of nickel can be detected in the presence of 400,000 parts of water. The reaction is not influenced by the presence of ten times as much cobalt; when a larger proportion of cobalt is present, the following procedure is recommended:

Detection of Traces of Nickel in Cobalt Salts

Add strong ammonia to the solution of the cobalt salt until a clear solution is obtained, then add a few cubic centimeters of hydrogen peroxide and boil the solution a few minutes to decompose the excess of this reagent. Then add the dimethylglyoxime and again bring the solution to a boil. A very small quantity of nickel causes a red scum to form and the glass sides of the beaker become coated with a film of red crystals. With smaller amounts of nickel the color is best observed upon the filter through which the solution is poured and the residue washed with hot water.

The above reaction is the most sensitive test known for detecting nickel in the presence of cobalt.

v. Fortini† recommends the following method for detecting nickel in alloys:

Heat the metal, from which all greasy or oily matter has been removed, at one spot with the oxidizing flame of the blowpipe. Cool and moisten with one drop of a solution of 0.5 gm. dimethylglyoxime in 5 cc. alcohol and 5 cc. concentrated ammonium hydroxide. A red spot at once appears if nickel is present. When copper is present, the nickel test is obtained before the copper ammonia color is visible.

14. **Ammonium Thioacetate** precipitates nickel sulfide from ammoniacal solution. In an acid solution, sodium thiosulfate has no effect but in neutral or alkaline solutions, nickel sulfide is slowly precipitated.

15. **Potassium Ferrocyanide** precipitates greenish nickelous ferrocyanide, $Ni_2[Fe(CN)_6]$ which is not very soluble in dilute hydrochloric acid.

16. **Potassium Ferricyanide** precipitates yellowish brown nickelous ferricyanide, $Ni_3[Fe(CN)_6]_2$. The precipitate is difficultly soluble in hydrochloric acid. In the presence of tartaric acid and a large excess

* *Ber.*, **38** (1905), 2520.

† *Chem. Ztg.* (**1912**), **1461.**

of ammonia, potassium ferricyanide forms a clear, brownish yellow solution.

17. **Potassium Thiocarbonate,** K_2CS_3, gives a dark brown coloration in a concentrated, ammoniacal solution of a nickel salt, or a reddish yellow color if the solution is dilute. This is a sensitive test for nickel; cobalt ions do not interfere but manganese and zinc ions are likely to interfere.

18. **Ammonium Molybdate** in neutral or slightly acid solutions of nickel salts causes a greenish white precipitation on heating to 70°.

19. **Potassium Chromate** reacts only slowly with a cold, neutral solution of a nickel salt. At the boiling temperature a chocolate-brown basic chromate, $NiCrO_4 \cdot NiO$, is formed which dissolves easily in acid or in ammonia water.

20. **α-Nitroso-β-naphthol,** dissolved in 50 per cent acetic acid gives a brown precipitate of the following composition: $[C_{10}H_6O(NO)]_2Ni$. The precipitate dissolves in hydrochloric acid.

21. **Dicyandiamidine Sulfate,** in 10 per cent aqueous solution, gives a yellow, crystalline precipitate of nickel dicyandiamidine, $(C_2H_5N_4O_2)Ni \cdot 2\,H_2O$. The reaction is a little slow in starting but the test is sensitive and characteristic. If the nickel solution is ammoniacal at the start, and contains ammonium chloride, then, after adding the reagent, the blue color is at once changed to yellow upon the addition of caustic soda and the precipitate forms gradually.

Reactions in the Dry Way

The borax, or sodium metaphosphate, bead is brown in the oxidizing flame, almost the same shade as the strongly saturated manganese bead; in the reducing flame the bead becomes gray, due to the formation of some metallic nickel. On looking at the bead through the microscope the finely divided metal can be seen suspended in the colorless glass.

On heating nickel salts with sodium carbonate on charcoal, a gray scale of metallic nickel is obtained. This reaction is best performed with the charcoal stick, as described on p. 66. The magnetic metal obtained in this way is placed on a piece of filter-paper, dissolved in nitric acid, a drop of concentrated hydrochloric acid is added, and the paper carefully dried by moving it back and forth over the flame. If nickel is present the paper appears greenish (colorless with very small amounts of nickel), or bluish if cobalt is also present. The paper is now moistened (where the nickel is) with caustic soda or potash, and is then held in bromine vapors, which are obtained by shaking some bromine water in a wide-mouthed flask.

If nickel or cobalt is present, a black spot will be formed by the above treatment, consisting of the hydroxide of the trivalent metal (p. 183). The blackening often does not appear at first; in this case the paper is moistened once more with potassium hydroxide and again treated with bromine. The spot will now appear if nickel is present.

COBALT, Co. At. Wt. 58.97

Sp. Gr. = 8.5. M. Pt. = 1490°

Occurrence. — Like nickel, native cobalt is found only in meteorites. It occurs in the earth's crust chiefly as sulfide, arsenide, and as salts of thioarsenious and thioantimonous acids; it is almost always accompanied by nickel and iron. The most important ores are smaltite, $CoAs_2$, isometric; cobaltite, CoAsS, isometric; skutterudite, $CoAs_3$, isometric; erythrite, $Co_3(AsO_4)_2 \cdot 8\,H_2O$, monoclinic, isomorphous with vivianite, $Fe_3(PO_4)_2 \cdot 8\,H_2O$, and with annabergite, $Ni_3(AsO_4)_2 \cdot 8\,H_2O$.

Metallic cobalt is steel gray, dissolves much more readily in dilute acids than nickel, and is, like the latter, magnetic. Cobalt forms, like iron, three oxides: cobaltous oxide, CoO; cobaltous cobaltic oxide, Co_3O_4; cobaltic oxide, Co_2O_3.

By dissolving these three oxides in acids, salts derived from cobaltous oxide are always obtained, containing bivalent cobalt:

$$CoO + 2\,HCl = H_2O + CoCl_2,$$
$$Co_2O_3 + 6\,HCl = 3\,H_2O + 2\,CoCl_2 + Cl_2\uparrow,$$
$$Co_3O_4 + 8\,HCl = 4\,H_2O + 3\,CoCl_2 + Cl_2\uparrow.$$

Simple cobaltic salts are unknown, but many complex compounds exist with trivalent cobalt, as, for example, potassium cobaltinitrite, potassium cobalticyanide, and numerous cobalti-ammonia derivatives.

Cobaltous compounds in a crystallized state (as well as in aqueous solution) are pink, in the anhydrous condition yellow or green, and blue in aqueous solutions in the presence of hydrochloric acid. The solubility reactions of cobaltous salts are similar to those of manganese and nickel.

Reactions in the Wet Way

1. **Potassium** or **Sodium Hydroxide** precipitates in the cold a blue basic salt:

$$Co^{++} + Cl^- + OH^- \rightarrow \mathbf{Co(OH)Cl},$$

which on warming is further decomposed by hydroxyl ions forming pink cobaltous hydroxide:

$$\mathbf{Co(OH)Cl} + OH^- \rightarrow Cl^- + \mathbf{Co(OH)_2}$$

In the case of a moderately concentrated solution of the alkali the precipitate of pink cobaltous hydroxide is often produced in the cold, sometimes only after standing some time. The rapidity of the reaction depends entirely upon the concentration of the alkali.

Cobaltous hydroxide gradually turns brown in contact with the air, going over into cobaltic hydroxide:

$$4\,Co(OH)_2 + 2\,H_2O + O_2 \rightarrow 4\,Co(OH)_3.$$

In this respect cobalt behaves similarly to iron and manganese, and differs from nickel, for the hydroxide of the latter is not oxidized by atmospheric oxygen.

On adding chlorine, bromine, hypochlorites, hydrogen peroxide, etc., to an alkaline solution containing cobaltous hydroxide, cobaltic hydroxide is immediately formed, as with nickel and manganese,

$$2\,Co(OH)_2 + 2\,OH^- + Cl_2 = 2\,Cl^- + 2\,Co(OH)_3,$$

$$2\,Co(OH)_2 + HOH + OCl^- = Cl^- + 2\,Co(OH)_3.$$

From ammoniacal cobalt solutions the above oxidizing agents cause no precipitation, but merely a red coloration; the addition of potassium hydroxide then causes no precipitation (difference from nickel).

The presence of non-volatile organic acids or of sugar prevents the precipitation of cobaltous and cobaltic hydroxides.

Cobaltous hydroxide, $CO(OH)_2$, behaves under some conditions as a weak acid, for on adding to a cobaltous solution a very concentrated solution of KOH or NaOH the precipitate at first produced dissolves with a blue color * similar to copper. By the addition of Rochelle salts to this blue cobalt solution the color either disappears almost entirely or becomes a pale pink, while the similarly treated copper solution becomes more intensely blue. By the addition of potassium cyanide to the blue cobalt solution it becomes yellow, and in contact with air turns intensely brown. A copper solution would be decolorized by the addition of potassium cyanide.

By pouring a little cobalt solution (or adding a little solid cobalt carbonate) into a concentrated solution of caustic soda or potash, to which a little glycerol has been added, a blue solution is formed (the color being intensified by warming), and after standing some time in the air, or immediately upon the addition of hydrogen peroxide, it becomes a beautiful green.

2. **Ammonia** precipitates, in the absence of ammonium salts, a blue basic salt, soluble, however, in excess of ammonium chloride. No precipitate is formed therefore, in solutions which contain sufficient ammonium chloride, but the dirty-yellow, ammoniacal solution gradually turns reddish on exposure to the air, owing to the formation of very stable cobalti-ammonia derivatives.

* Ed. Donath, *Z. anal. Chem.*, **40** (1901), 137.

3. **Alkali Carbonates** produce a reddish precipitate of basic salt of varying composition.

4. **Ammonium Carbonate** also precipitates a reddish basic salt, soluble, however, in excess.

5. **Barium Carbonate** precipitates no cobalt in the cold and out of contact with air, but on exposure to the air cobaltic hydroxide is gradually thrown down. The precipitation takes place much more quickly on the addition of hypochlorites or hydrogen peroxide:

$$2\,Co^{++} + 2\,BaCO_3 + 3\,H_2O + OCl^- \rightarrow 2\,Ba^{++} + Cl^- + 2\,Co(OH)_3 + 2\,CO_2\uparrow.$$

If the solution is heated to boiling, all of the cobalt is precipitated as a basic salt, even out of contact with the air.

6. **Hydrogen Sulfide** produces no precipitate in solutions containing mineral acids. In neutral solutions containing an alkali acetate all of the cobalt is precipitated as black sulfide.

7. **Ammonium Sulfide** precipitates black cobalt sulfide,

$$Co^{++} + S^{--} \rightarrow CoS,$$

insoluble in ammonium sulfide, acetic acid, and very dilute hydrochloric acid (cf. p. 184); soluble in concentrated nitric acid and aqua regia, with separation of sulfur:

$$3\,CoS + 8\,HNO_3 = 4\,H_2O + 2\,NO\uparrow + 3\,S + 3\,Co(NO_3)_2.$$

By continued action of strong nitric acid all the sulfur goes into solution as sulfuric acid.

The addition of an oxidizing agent always helps an acid to dissolve an insoluble sulfide. The solution in contact with a sulfide precipitate at first contains enough sulfide ions to satisfy the solubility product of the sulfide. When hydrogen ions are added nonionized hydrogen sulfide is formed unless the solubility-product of the sulfide is so small that less sulfide ions are present than would be formed by the ionization of H_2S. If an appreciable quantity of H_2S is formed, it can be expelled as a gas and the sulfide will dissolve. Sometimes, however, this takes place very slowly and then the addition of an oxidizing agent is necessary. The sulfide ions in solution are oxidized to free sulfur. The solubility-product of the sulfide is no longer reached in solution, for as fast as a little of the substance dissolves the sulfide ions are oxidized.

8. **Potassium Cyanide** produces in neutral solutions a reddish-brown precipitate, soluble in excess of potassium cyanide in the cold, with a brown color, forming potassium cobaltocyanide:

$$Co^{++} + 2\,CN^- \rightarrow Co(CN)_2;\quad CoCN_2 + 4\,CN^- \rightarrow [Co(CN)_6]^{----}.$$

On warming the brown solution for some time it becomes bright yellow and reacts alkaline; it now contains potassium cobalticyanide,

of analogous composition to potassium ferricyanide. The formation of the cobaltic salt takes place with the help of atmospheric oxygen:

$$4\,[Co(CN)_6]^{--} + O_2 + 2\,H_2O \rightarrow 4\,[Co(CN)_6]^{---} + 4\,OH^-.$$

The reaction takes place more quickly in the presence of chlorine, bromine, hypochlorites, etc.:

$$2\,[Co(CN)_6]^{--} + Cl_2 \rightarrow 2\,[Co(CN)_6]^{---} + 2\,Cl^-.$$

An excess of chlorine, bromine, etc., does not decompose the cobaltic salt (difference from nickel).

The cobalticyanide anion is much more stable than the cobaltocyanide anion. By adding hydrochloric acid to the brown solution of potassium cobaltocyanide, hydrogen cyanide will be set free and yellow cobaltous cyanide formed,

$$[Co(CN)_6]^{--} + 4\,H^+ \rightarrow 4\,HCN + \mathbf{Co(CN)_2'},$$

while potassium cobalticyanide is not decomposed by hydrochloric acid.

Potassium cobalticyanide forms, with most of the heavy metals, difficultly soluble or insoluble salts possessing characteristic colors. Thus, it produces with cobaltous salts pink cobaltous cobalticyanide:

$$2\,[Co(CN)_6]^{---} + 3\,Co^{++} \rightarrow \mathbf{Co_3[Co(CN)_6]_2},$$

and with nickel salts greenish nickelous cobalticyanide.

If, therefore, a cobalt solution contains nickel it gives, on precipitating and redissolving with potassium cyanide, boiling, and adding hydrochloric acid, a greenish precipitate of nickelous cobalticyanide:

$$2\,[Co(CN)_6]^{---} + 3\,[Ni(CN)_4]^{--} + 12\,H^+ \rightarrow 12\,HCN + \mathbf{Ni_3[Co(CN)_6]_2}.$$

If potassium nitrite and acetic acid are added to a solution of potassium cobaltocyanide, the liquid becomes blood-red in color owing to the formation of potassium nitrocobalticyanide, $K_4Co_2(CN)_9NO_2 \cdot 3\,H_2O$.

If a solution of potassium cobaltocyanide is shaken with sodium hydroxide, it becomes brown and on adding yellow ammonium sulfide a blood-red coloration is obtained.

9. **Potassium Nitrite** produces in concentrated solutions of cobalt salts, with the addition of acetic acid, an immediate precipitation of yellow, crystalline potassium cobaltinitrite. If the solution is dilute, the precipitate appears only after standing for some time, but more quickly on rubbing the sides of the beaker.

$$Co^{++} + 7\,NO_2^- + 3\,K^+ + 2\,H^+ \rightarrow NO + H_2O + \mathbf{K_3[Co(NO_2)_6]}.$$

This reaction offers an excellent means for detecting the presence of cobalt in nickel salts.

10. **Ammonium Thiocyanate** *(Vogel's reaction).** *If a concentrated solution of ammonium thiocyanate is added to a cobaltous solution, the latter becomes a beautiful blue, owing to the formation of ammonium cobaltothiocyanate:*

$$Co^{++} + 4\,CNS^- + 2\,NH_4^+ \rightarrow (NH_4)_2[Co(CNS)_4].$$

On adding water the blue color disappears and the pink color of the cobaltous salt takes its place. If amyl alcohol† is added (or a mixture of equal parts amyl alcohol and ether), and the solution shaken, the upper alcoholic layer is colored blue. This reaction is so sensitive that the blue color is recognizable when the solution contains only 0.0002 mg. of cobalt. The blue solution also shows a characteristic absorption spectrum.‡ Nickel salts produce no coloration of the amyl alcohol. If, however, iron is present, red $Fe(CNS)_3$ is formed, which likewise colors the amyl alcohol, making the blue color (due to the cobalt) very indistinct, so that, under some conditions, it can no longer be detected. If, however, 2 or 3 cc. of concentrated ammonium acetate solution and 2 or 3 drops of 50 per cent tartaric acid solution are added, the red color produced by $Fe(CNS)_3$ will disappear and the blue color of the cobalt compound will be seen.

The blue color is probably that of undissociated $(NH_4)_2[Co(CNS)_4]$. When the solution is diluted, the salt is ionized and the complex anion also is in equilibrium with cobalt ions, the more dilute the solution, the greater the ionization (cf. p. 18). The alcohol and ether probably dissolve only the undissociated $(NH_4)_2[Co(CNS)_4]$ and this is evidently present to some extent in the aqueous solution, although its color is obscured by that of cobaltous ions.

11. **Ether Saturated with Hydrogen Chloride** does not precipitate an anhydrous cobaltous salt, as in the case of nickel, but will dissolve the blue, anhydrous cobaltous chloride. This furnishes a basis of a method for separating nickel and cobalt.

12. **α-Nitroso-β-naphthol,** $C_{10}H_6(NO)OH$, produces a voluminous, purple red precipitate of cobalti-nitroso-β-naphthol, $[C_{10}H_6(NO)O]_3Co$, which is insoluble in cold, dilute nitric or hydrochloric acid.§

This reagent serves not only for qualitative purposes, but can also be used for the quantitative determination of cobalt in the presence of nickel. The test may be applied conveniently to the solution obtained in the usual qualitative scheme after the removal of all metals except nickel and cobalt. A part of the solution may be

* *Ber.*, **12**, 2314; Treadwell, *Z. anorg. Chem.*, **26** (1901), 105.

† T. T. Morrell first showed that cobalt salts give a blue color with ammonium thiocyanate, disappearing on the addition of water, but reappearing when alcohol is added. *Z. anal. Chem.*, **16**, 251.

‡ Wolff, *Z. anal. Chem.*, **18**, 58.

§ Ilinski and v. Knorre, *Ber.*, **18**, 699 (1885).

used for the sensitive nickel test with dimethylglyoxime (p. 185) and the remainder used for the cobalt test.

Dilute the solution to about 50 cc., add 4 cc. of 6 N hydrochloric acid and 20 cc. of 6 N acetic acid. Heat, add 50 cc. of a saturated solution of nitroso-β-naphthol in 50 per cent acetic acid and boil. If as much as 0.1 mg. of cobalt is present, a red precipitate or turbidity is obtained even in the presence of 250 mg. of nickel. When more than 150 mg. of nickel is present, however, some of the brownish-yellow nickel compound, $(C_{10}H_6(NO)O)_2Ni$, will precipitate after the solution cools.

The reagent used in this test should be freshly prepared. Nitroso-β-naphthol gradually decomposes on standing in the air and changes from yellow to brown or even black in color. It can be purified by dissolving in hot sodium carbonate, filtering and reprecipitating with sulfuric acid. For all ordinary purposes the saturated solution in 50 per cent acetic acid is most suitable. The cobalt test can be made more delicate by adding an equal volume of alcohol to the test and, for detecting traces of cobalt, an aqueous solution of the organic substance can be used, but as 5000 cc. of water are required to dissolve 1 gm. of the nitroso-β-naphthol, it is evident that the aqueous solution is not suitable when much cobalt is present. An excess of the reagent is required, as a part of it is used to oxidize the cobalt to the trivalent condition.

Copper gives a characteristic coffee-brown precipitate with the reagent and it is possible to separate copper from lead, cadmium, etc., by means of it. Ferric iron gives a brownish-black precipitate which is insoluble enough to serve as a means of separating iron from aluminium, manganese, etc. Ferrous iron also gives a greenish precipitate in neutral solutions. Of all these precipitates, however, the cobalt compound is the most characteristic and the least influenced by the presence of acid. Thus with the acidity recommended above, the presence of a little ferric or ferrous iron causes no disturbance.

13. **Ammonium Thioacetate** precipitates cobaltous sulfide from ammoniacal solutions. Sodium thiosulfate has no action upon acid solutions, and in neutral solutions an incomplete precipitation of cobaltous sulfide is obtained.

14. **Potassium Ferrocyanide,** precipitates green cobaltous ferrocyanide, $Co_2[Fe(CN)_6]$, difficultly soluble in hydrochloric acid.

15. **Potassium Ferricyanide** precipitates brownish red cobaltous ferricyanide, $Co_3[Fe(CN)_6]_2$ scarcely soluble at all in hydrochloric acid. If tartaric acid or ammonium chloride and an excess of ammonia are added to a solution of a simple cobalt salt, a clear solution is obtained; the addition of ferricyanide causes a yellowish red coloration. This sensitive reaction has been recommended for the detection of cobalt in the presence of nickel.

16. **Potassium Thiocarbonate,** K_2CS_3, added to an ammoniacal cobalt solution gives a brownish or black color if much cobalt is present, and a wine-yellow color with very little cobalt.

17. **Potassium Chromate** gives a brownish-red precipitate of basic cobaltous chromate, $CoCrO_4 \cdot CoO \cdot H_2O$. The precipitate dissolves in acids and in ammonia water.

18. **Dimethylglyoxime** gives no precipitate with an ammoniacal cobalt solution but a wine-red color is obtained if hydrogen sulfide or ammonium sulfide is also present.

19. **Dicyandiamidine Sulfate** gives no precipitate in ammoniacal cobalt solutions upon the addition of sodium hydroxide. If a sufficient quantity of cane sugar is added a complex ion is formed with the sugar and there is no danger of precipitating cobalt hydroxide with the sodium hydroxide. This complex has a deep red color. This red color can be seen after the precipitation of nickel with dicyandiamidine sulfate.

Detection of Traces of Cobalt in Nickel Salts

To test a nickel salt for cobalt, add a concentrated solution of ammonium thiocyanate to the solution of a considerable amount of the salt, a few cubic centimeters of amyl alcohol and ether and shake the mixture. After settling, if the upper alcohol-ether layer is colorless, then the nickel salt contains neither iron nor cobalt; if the layer is reddish, iron is present. In the latter case add 2 or 3 cc. of concentrated ammonium acetate solution and 2 or 3 drops of 50 per cent tartaric acid solution and shake again; if cobalt is present the alcohol-ether layer is now distinctly blue.

Sometimes when very little cobalt and considerable nickel is present it is difficult to tell whether the amyl alcohol is colored blue or not. In that case pour the solution into a separatory funnel and draw off the lower layer containing the green nickelous solution. Add a little more ammonium thiocyanate solution to the amyl alcohol, 1 cc. of ammonium acetate solution, 1 drop of tartaric acid solution and shake again. The blue color should now appear if any cobalt is present.

Reactions in the Dry Way

The bead produced by borax or sodium metaphosphate is blue in both the oxidizing and reducing flames. By holding the bead in the upper reducing flame for a long time it is possible to reduce the cobalt to metal, when it appears, like nickel, gray.

On the charcoal stick cobalt compounds yield gray metallic cobalt, which can be removed by means of a magnetized knife-blade placed on filter paper, dissolved in hydrochloric acid and dried, as described on p. 67. The paper is then colored blue by cobalt (difference from nickel). If, now, sodium hydroxide is added and the paper exposed to the action of bromine vapors, black cobaltic hydroxide, $Co(OH)_3$, is formed.

ZINC, Zn. At. Wt. 65.37

Sp. Gr. = 6.9. M. Pt. = 419°. B. Pt. = 916°

Occurrence. — Smithsonite, $ZnCO_3$, isomorphous with calcite, $CaCO_3$, etc.; sphalerite, ZnS, isometric; calamine, $Zn_2SiO_4 + H_2O$, orthorhombic, hemimorphic; zincite, ZnO, hexagonal; and franklinite, $(FeO_2)_2(Fe,Mn,Zn)$, isometric.

The most important zinc ore is sphalerite, ZnS. Sulfide of zinc is dimorphic and is also found as wurtzite, which crystallizes in the hexagonal system.

Metallic zinc is bluish white. At low temperatures and at about 200° C. it is so brittle that it can be pulverized, but at 110°–150° C. it is ductile and can be drawn out into wire and rolled into foil.

Zinc, as its position in the electromotive series indicates (p. 41), dissolves readily in all acids; in hydrochloric,* sulfuric, and acetic acids with evolution of hydrogen:

$$Zn + 2\,H^+ \rightarrow Zn^{++} + H_2\uparrow.$$

Zinc is such a strong reducing agent that it easily reduces nitric acid, the extent of the reduction depending upon the concentration of the acid. With very concentrated acid, some NO_2 is obtained, while dilute acid is reduced to ammonium nitrate. In ordinary acid the principal product is nitric oxide, NO.

$$3\,Zn + 8\,HNO_3 \rightarrow 3\,Zn^{++} + 6\,NO_3^- + 4\,H_2O + 2\,NO\uparrow.$$
$$4\,Zn + 10\,HNO_3 \rightarrow 4\,Zn^{++} + 8\,NO_3^- + NH_4NO_3 + 3\,H_2O.$$

Like aluminium, zinc dissolves in caustic soda or potash, with evolution of hydrogen and the formation of a zincate:

$$Zn + 2\,OH^- \rightarrow ZnO_2^{--} + H_2\uparrow.$$

Zinc forms only one oxide, ZnO. It is a white infusible powder, which becomes yellow when heated, but turns white again on cooling. Zinc oxide dissolves readily in acids, forming zinc salts:

$$ZnO + H_2SO_4 = H_2O + ZnSO_4.$$

There exists only one series of zinc salts, and the zinc is always bivalent. Most of the salts are white. The chloride, nitrate, sulfate, and acetate are soluble in water; the remainder dissolve readily in mineral acids.

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* Absolutely pure zinc dissolves very slowly in these acids but the metal dissolves readily if a trace of some metal lower in the electromotive series is present.

Reactions in the Wet Way

1. **Potassium** or **Sodium Hydroxide** precipitates white, gelatinous zinc hydroxide, easily soluble in excess of the precipitant, forming a zincate: *

$$Zn^{++} + 2\,OH^- \rightarrow \mathbf{Zn(OH)_2};\ \mathbf{Zn(OH)_2} + OH^- \rightleftarrows HZnO_2^- + H_2O.$$

Zinc hydroxide, like aluminium hydroxide, behaves sometimes as a base and sometimes as an acid.

On boiling a dilute solution of a zincate, hydrolysis takes place and zinc hydroxide is precipitated, but if the solution contains an excess of OH^- ions, there is no precipitation.

2. **Ammonia** precipitates from neutral solutions, free from ammonium salts, zinc hydroxide, readily soluble in ammonium salts, as in the case of magnesium, nickel, manganese, or iron:

$$Zn^{++} + 2\,NH_4OH \rightleftarrows \mathbf{Zn(OH)_2} + 2\,NH_4^+.$$

Zinc hydroxide is also soluble in an excess of ammonia, due to the formation of complex zinc ammonia ions:

$$\mathbf{Zn(OH)_2} + 6\,NH_3 \rightarrow [Zn(NH_3)_6]^{++} + 2\,OH^-.$$

3. **Alkali Carbonates** precipitate a white, basic carbonate, of variable composition, as with magnesium.

4. **Ammonium Carbonate** does the same, except that the precipitate is soluble in an excess of the reagent. The presence of ammonium salts or of ammonia prevents the precipitation.

5. **Barium Carbonate** precipitates no zinc in the cold, but on boiling all the zinc is precipitated as basic carbonate.

6. **Sodium Phosphate** precipitates gelatinous, tertiary zinc phosphate, which soon becomes crystalline, and is soluble in ammonia and in acids:

$$3\,Zn^{++} + 4\,HPO_4^{--} \rightarrow 2\,H_2PO_4^- + \mathbf{Zn_3(PO_4)_2}.$$

In the presence of ammonium salt, the less soluble zinc ammonium phosphate is precipitated:

$$Zn^{++} + NH_4^+ + 2\,HPO_4^{--} \rightarrow H_2PO_4^- + \mathbf{ZnNH_4PO_4}.$$

Both zinc phosphate and zinc ammonium phosphate dissolve readily in dilute acids, owing to the formation of very slightly ionized HPO_4^{--}, and in dilute ammonia, owing to the formation of zinc ammonia cations.

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* According to HANTZSCH the zinc is not present as zincate, but probably in colloidal solution. *Z. anorg. Chem.*, **30**, 289 (1902). In fairly concentrated solutions, however, it is certain that the zinc is present as zincate, for F. FOERSTER and O. GÜNTHER, *Z. Electrochem.*, **6**, 301 (1900), have isolated the compound, $NaHZnO_2 \cdot 3\,H_2O$, as needles with silky luster.

Acids, therefore, deprive the solution of PO_4^{---} anions by forming HPO_4^{--}, and ammonia deprives the solution of zinc ions by forming $[Zn(NH_3)_6]^{++}$.

7. **Hydrogen Sulfide** precipitates the zinc as sulfide, from neutral solutions of a zinc salt:

$$Zn^{++} + H_2S \rightleftarrows ZnS + 2\,H^+.$$

The solubility product of zinc sulfide (p. 22) is about 1.2×10^{-23}. At 25° the concentration of a saturated solution of hydrogen sulfide is about 0.1 molar and the ionization constant for the complete ionization, $H_2S \rightleftarrows 2\,H^+ + S^{--}$, has been estimated to be 1.1×10^{-23}. The concentration of the sulfide ion in such a solution is approximately 1.2×10^{-15} molar equivalents per liter. The solubility-product of zinc sulfide is evidently exceeded when the aqueous solution of a zinc salt is saturated with hydrogen sulfide and zinc sulfide is precipitated. The mass-action principle applied to the complete ionization of hydrogen sulfide shows that the concentration of sulfur ions is inversely proportional to the square of the concentration of the hydrogen ions. If the concentration of the hydrogen ions is increased one thousandfold, and this is approximately the case when the solution is tenth-normal with a mineral acid, the concentration of the sulfide ions from hydrogen sulfide is reduced to one-millionth of its value in pure water.

The separation of the second group of metals from the third group is usually accomplished by passing hydrogen sulfide into a solution which is about 0.3-normal with hydrochloric or nitric acid. The concentration of the sulfide ion when such a solution is saturated with hydrogen sulfide at 25° is about 1.1×10^{-22}. To reach the solubility product of zinc sulfide in 0.3-normal acid, the zinc ions should reach the concentration of about 0.11 mole per liter, or about 0.7 gm. per 100 cc.*

If the zinc salt has a greater concentration than this, some zinc sulfide may be precipitated by hydrogen sulfide in 0.3-normal acid solution. The precipitation would evidently be incomplete, for, as more hydrogen ions are formed in solution from the hydrogen sulfide as a result of the sulfide precipitation, the ionization of the hydrogen sulfide continually tends to become less.

If, however, considerable sodium or ammonium acetate is added to the acid solution, the concentration of the hydrogen ion becomes much smaller and the ionization of the hydrogen sulfide takes place to a greater extent. It is then possible to precipitate the zinc as sulfide so completely that less than 1 mg. of zinc will remain in solution.

Zinc sulfide dissolves readily in normal hydrochloric acid. The sulfur ions from the zinc sulfide enter into equilibrium with the hydrogen ions of the acid to form hydrogen sulfide. In normal acid solution, the concentration of sulfur ions from saturated hydrogen sulfide is about 1.2×10^{-23} and of sulfur ions from a saturated solution of ZnS in water about 3.5×10^{-12}.

8. **Ammonium Sulfide** precipitates from neutral or alkaline solutions all the zinc as amorphous sulfide:

$$Zn^{++} + S^{--} \rightarrow ZnS.$$

* This value is merely an approximation, being derived by a rough calculation from values which are not very reliable.

Zinc sulfide is a precipitate difficult to filter; it runs through the filter-paper, particularly on washing. This is a peculiarity of most all metallic sulfides and of many other amorphous bodies, such as aluminium hydroxide, titanic acid, tungstic acid, and many others. This is due to its tendency to form colloidal solutions (p. 57). The colloid can be precipitated by adding a concentrated salt solution or by boiling.

In order, then, to obtain zinc sulfide in a form which can be filtered, it is best precipitated from a boiling solution containing acetic acid and a considerable quantity of ammonium salts. The precipitate may be washed with a solution of ammonium chloride to which a little ammonium sulfide has been added.

9. **Potassium Cyanide** produces a white precipitate of zinc cyanide, soluble in an excess of the precipitant.

$$Zn^{++} + 2\,CN^- \rightleftarrows \mathbf{Zn(CN)_2};\ \mathbf{Zn(CN)_2} + 2\,CN^- \rightarrow [Zn(CN)_4]^{--}.$$

The zinc-cyanide anion is decomposed by acids and by alkali sulfide:

$$[Zn(CN)_4]^{--} + 2\,H^+ \rightarrow \mathbf{Zn(CN)_2} + 2\,HCN;$$

$$[Zn(CN)_4]^{--} + S^{--} \rightarrow \mathbf{ZnS} + 4\,CN^-.$$

10. **Potassium Ferrocyanide** precipitates white zinc ferrocyanide, which is changed by an excess of the potassium ferrocyanide into less soluble zinc-potassium ferrocyanide:

$$[Fe(CN)_6]^{----} + 2\,Zn^{++} \rightarrow \mathbf{Zn_2[Fe(CN)_6]}$$

$$3\,\mathbf{Zn_2[Fe(CN)_6]} + K_4[Fe(CN)_6] \rightarrow 2\,\mathbf{K_2Zn_3[Fe(CN)_6]_2}.$$

By treatment with bromine, the precipitate is changed into a yellow oxidation product.

11. **Ammonium Thioacetate** precipitates ZnS from ammoniacal solutions but not from acid solutions. Sodium thiosulfate has no effect.

12. **Potassium Ferricyanide** precipitates brownish-yellow zinc ferricyanide, $Zn_3[Fe(CN)_6]_2$, soluble in hydrochloric acid and in ammonia.

13. **Potassium Periodate** gives a white precipitate in aqueous solutions. The presence of ammonium chloride tends to prevent the precipitation in the cold but on boiling all the zinc is thrown down.

14. **Electrolysis** of an alkaline zincate solution with a copper wire (0.5 mm. thick) as cathode in a small cell, enables one to detect an extremely small quantity of zinc by the appearance of the wire.

Reactions in the Dry Way

Heated with sodium carbonate on charcoal before the blowpipe, it is not possible to obtain metallic zinc on account of its volatility; but an incrustation of oxide is obtained which is yellow while hot and white when cold.

Zinc oxide (or such compounds of zinc as are changed over to oxide on ignition) when moistened with cobalt nitrate and ignited, yields a green infusible mass — Rinnmann's green. This reaction is performed exactly as with aluminium (p. 139).

Separation of the Metals of Group III from the Alkalies and Alkaline Earths

The separation of the members of the ammonium-sulfide group from the alkalies and alkaline earths is effected by means of ammonium sulfide and ammonium chloride. If, however, the solution contains phosphoric acid, oxalic acid, or considerable boric acid, the neutralization of the solution will cause the precipitation of calcium, strontium, barium, and magnesium as phosphate, oxalate, or borate. Hydrofluoric acid causes precipitation of calcium fluoride in this group. The procedure to be followed when such acids are present will be given in Part IV of this book after the characteristic properties of the acids have been described in Part III. Method B will also show a simple modification which can be followed when phosphate is present.

A number of excellent schemes have been devised for the analysis of this group and each has something in its favor. In this book it has seemed best not to attempt to decide upon a single scheme, but rather to treat the subject in a broader manner, partly because of the instructive value of studying several schemes and partly because one scheme is best under certain conditions and another scheme under different conditions. Thus it is a quite common practice to divide the whole group into two minor groups, one containing ferric iron, aluminium, chromium, and uranium and the other containing manganese, nickel, cobalt and zinc. Such a scheme often works very nicely and enables one to arrive at proper conclusions quickly but, unfortunately, chromium when precipitated in this way has a marked tendency to carry down zinc and magnesium with it, and this may result in the failure to detect zinc or magnesium during the subsequent examination. Chromium, however, on account of the color of its compounds, invariably betrays its presence before the actual test for chromium is made, and it is a very easy matter to modify the method somewhat when chromium is present in order that zinc and magnesium will not be missed. It is unnecessary to use such a modified method when chromium is known to be absent. In most schemes of analysis the detection of uranium and titanium is not provided for in the analysis of this group. Titanium, although present in most rocks, is usually found in very small quantities. When much titanium is present, this fact is known by the difficulty involved in getting the substance in solution and the tendency of the dilute acid solutions to hydrolyze and form precipitates of metatitanic acid, which are difficult to filter. When much titanium is present it is precipitated according to p. 167, § 4. To detect small quantities of titanium, the hydrogen peroxide test (p. 168) is most suitable. Uranium is of relatively rare occurrence, but its ores have become important since the discovery of radium in them. The detection of uranium will be included in the first of the schemes of analysis that follow.

TABLE VII. — ANALYSIS OF GROUP III IN ABSENCE OF PHOSPHATE

METHOD A

Solution may contain: Fe+++, Fe++, UO_2++, Al+++, Cr+++, Mn++, Zn++, Co++, Ni++, also Groups IV and V. *Add NH_4OH and $(NH_4)_2S$. Filter and examine filtrate for Groups IV and V. Treat ppt. with 2-normal HCl.* (2)

Residue: CoS, NiS. *Test for Ni and Co by bead test. Test for Ni with dimethylglyoxime and for cobalt with ammonium thiocyanate.* (3)

Solution: Fe++, UO_2++, Al+++, Cr+++, Mn++, Zn++ [and some Ni]. *Add NaOH in excess.* (4)

Precipitate: $Fe(OH)_3$, $Cr(OH)_3$, $Na_2U_2O_7$, $Mn(OH)_2$ [and some $Ni(OH)_2$]. *Dissolve in HCl, add NH_4Cl and NH_4OH.* (5)

Filtrate: AlO_2^-, $HZnO_2^-$. *Add HCl and then NH_4OH.* (10)

Precipitate: $Fe(OH)_3$, $Cr(OH)_3$, $(NH_4)_2U_2O_7$. *Dissolve in HCl and add excess $(NH_4)_2CO_3$.* (6)

Filtrate: Mn++ (and Ni++). *Test for Mn by $(NH_4)_2S$ by $NaBiO_3$ or by fusion with Na_2CO_3 and KNO_3.* (9)

Precipitate: $Al(OH)_3$. *Confirm by Thénard's blue test.* (10)

Filtrate: Zn++. *Acidify with $HC_2H_3O_2$ add H_2S and confirm Zn by Rinnmann's green test.* (11)

Precipitate: $Fe(OH)_3$, $Cr(OH)_3$. *Test for Fe with $K_4Fe(CN)_6$.* Test for Cr by fusion with Na_2CO_3 and KNO_3, etc. (7)

Filtrate: $(NH_4)_4UO_2(CO_3)_3$ *Acidify with HCl and test with $K_4Fe(CN)_6$.* (8)

PROCEDURE METHOD A

1. Heat the neutral solution to boiling, add 5 cc. of normal ammonium chloride solution, if this salt is not already present, and ammonium sulfide solution drop by drop until no further precipitation takes place. Avoid adding an excess of ammonium sulfide on account of the danger of getting a turbid filtrate when nickel is present. (To avoid this danger it is well to pass hydrogen sulfide into the slightly ammoniacal solution instead of adding ammonium sulfide. The reason why nickel sulfide runs through the filter is partly because ammonium polysulfide is present to some extent in the ammonium sulfide reagent that is not freshly prepared.) Filter off the precipitated sulfides and wash promptly with hot water. If the moist sulfides are allowed to stand exposed to the air, some sulfate is formed by oxidation and this will dissolve in the wash water. Reject all but the first washings and use the filtrate for the analysis of the alkaline earth and alkali groups (p. 118 *et seq.*).

2. Digest the precipitated sulfides in a porcelain dish with cold, 2-normal hydrochloric acid, stirring until no more hydrogen sulfide is evolved. Filter off the resi-

due, which consists chiefly of cobalt and nickel sulfides and wash with a little hydrochloric acid. Usually a partial oxidation of the sulfide takes place during this treatment with dilute acid and sulfur is formed which is likely to enclose a little sulfide that should dissolve in the acid. The fact that a residue remains is not, therefore, positive proof of the presence of nickel or cobalt. Examine the solution by § 4.

3. Test the residue for cobalt by heating a little of it in a borax bead; a blue bead shows *cobalt*. If the borax bead is brown, further test for nickel is unnecessary. If a blue bead is obtained, test for *nickel* by dissolving the precipitate in aqua regia, evaporating just to dryness, adding a little water and testing with dimethylglyoxime and ammonia (p. 185). If a brown bead is obtained, dissolve the precipitate as just described and, to the solution freed from mineral acid, add a concentrated solution of potassium nitrite, acidify with acetic acid and allow the solution to stand at least ten minutes. A fine yellow precipitate of $K_3[Co(NO_2)_6]$ shows that *cobalt* is present.

4. Evaporate the solution obtained in (2) to a small volume, oxidize any iron present to the ferric condition by heating with a little strong nitric acid, then add sodium hydroxide solution until a strongly alkaline solution is obtained, boil and filter. Examine the filtrate by § 10.

The precipitate may contain iron, chromium, uranium and manganese (with a little nickel) and the filtrate may contain aluminium and zinc.

5. Dissolve the precipitate in as little hydrochloric acid as possible, dilute the solution with hot water and boil several minutes. Add 5 cc. of ammonium chloride solution, make barely alkaline with ammonia and filter promptly. The precipitate contains all the iron, chromium and uranium; the filtrate, which may contain manganese, and traces of nickel, is analyzed by § 9.

6. Dissolve the precipitate in as little hydrochloric acid as possible, add a large excess of ammonium carbonate solution, heat gently but do not boil long, and filter. The precipitate contains the iron and chromium; the filtrate contains uranium in solution as ammonium uranyl carbonate. Test the latter by § 8.

7. Test the precipitate obtained in (6) for iron by dissolving a part of it in a few drops of hydrochloric acid, diluting with a little water and adding potassium ferrocyanide solution. The formation of Prussian blue shows the presence of *iron*. Test another portion of the precipitate for chromium by mixing it with sodium carbonate and potassium nitrate and fusing to form sodium chromate. Dissolve the melt, which is yellow if chromium is present, in water, acidify the aqueous extract with acetic acid and add a drop of silver nitrate solution; a red precipitate of silver chromate is formed if *chromium* is present.

8. To test for *uranium*, add hydrochloric acid to the solution obtained in (6) and treat the slightly acid solution with potassium ferrocyanide; a brown precipitate shows the presence of *uranium*.

9. Test the filtrate from (5) for *manganese*. Evaporate the solution to dryness, dissolve the residue in a little water and add a few drops of potassium cyanide solution. Dilute with water, add ammonium sulfide and boil. A flesh-colored precipitate is MnS. To confirm the test, dissolve a portion of the precipitate in concentrated nitric acid, add a little lead peroxide and boil. Dilute with water and allow the precipitate to settle; *manganese* is shown by the characteristic color of the permanganate ion. Or, a small portion of the manganous sulfide can be fused with sodium carbonate and potassium nitrate. A green melt shows the presence of *manganese*.

10. Test the filtrate obtained from (4) for *aluminium* and *zinc*. Make it acid with hydrochloric acid and then add a slight excess of ammonia. A white precipitate is $Al(OH)_3$; often silicic acid (from the action of reagents on glass) is precipitated here. Filter and test the filtrate for zinc (11). To confirm the aluminium test, dissolve the precipitate or a small portion of it in nitric acid and add half as many drops of 1 per cent cobaltous nitrate solution as there are presumable milligrams of aluminium in the precipitate and evaporate the solution nearly to dryness in a casserole. Soak up the solution in a small piece of filter paper, roll up the paper and wind a platinum wire around it. Heat in the flame till all the paper is consumed and then ignite strongly. Thénard's blue shows the presence of *aluminium* (p. 131).

11. To test for *zinc*, acidify the solution obtained in (10) with acetic acid and saturate it with hydrogen sulfide. Filter and dissolve the precipitate in a little nitric acid. Add 1 to 3 drops of 0.3-normal cobalt nitrate solution, evaporate to dryness and ignite the contents of the dish until the purple color of the cobalt salt disappears. Rinnmann's green (p. 199) shows the presence of *zinc*.

TABLE VIII. — ANALYSIS OF GROUP III IN ABSENCE OF PHOSPHATE

METHOD B *

Solution may contain Fe++, Fe+++, Al+++, Cr+++, Mn++, Zn++, Co++, Ni++, an Groups IV and V.

Add NH_4OH and $(NH_4)_2S$. Filter and examine filtrate for Groups IV and V (p. 118 or p. 120 *Dissolve ppt. in HCl and $KClO_3$. Evaporate, treat with NaOH and Na_2O_2 and filter.* (2)

Precipitate: $Fe(OH)_3$, H_2MnO_3, $Co(OH)_3$, $Ni(OH)_2[Zn(OH)_2]$. *Dissolve in HNO_3 and H_2O_2. Evaporate and boil with conc. HNO_3+$KClO_3$.* (3)

Filtrate: AlO_2^-, CrO_4^{--} $HZnO_2^-$. *Acidify with HCl an add NH_4OH.* (12)

Precipitate: MnO_3. *Dissolve in HNO_3 + H_2O_2 and test for Mn with $NaBiO_3$.* (4)

Filtrate: Fe+++, Co++, Ni++, [Zn++]. *Add NH_4OH.* (5) *If phosphate is present, proceed as outlined in* (6).

Precipitate: $Fe(OH)_3$. *Test for Fe with $K_4Fe(CN)_6$.* (5 or 6)

Filtrate: $Co(NH_3)_6$++, $Ni(NH_3)_6$++, $[Zn(NH_3)_6$++]. *Saturate with H_2S and treat ppt. with cold, normal HCl.* (7)

Residue: CoS,NiS. *Dissolve in HCl and $KClO_3$ and evaporate just to dryness. Add $HC_2H_3O_2$ and KNO_2 to precipitate cobalt as yellow $K_3[Co(NO_2)_6]$. Filter and test the filtrate with dimethylglyoxime.* Red precipitate of $Ni[(CH_3C{=}NO)_2H]_2$ shows the presence of nickel. (8)

Solution: Zn++, traces of Co++ and Ni++. *Add NaOH and Na_2O_2.* (9)

Precipitate: $Co(OH)_3$ $Ni(OH)_2$. *Add to residue of CoS, NiS.* (10)

Filtrate: Na_2ZnO_2. *Acidify with $HC_2H_3O_2$ and saturate with H_2S. Confirm Zn as in Method A.* (11)

Precipitate: Al$(OH)_3$. *Dissolve in HNO_3,* add $Co(NO_3)_2$ solution and NH_4OH. *Filter and ignite the residue.* Thenard's blue shows the presence of Al. (13).

Filtrate: $Zn(NH_3)_6$+ CrO_4^{--}. *Boil with Na_2CO_3, till all NH_3 expelled.* (14)

Precipitate: $Zn_3(OH)_2CO_3$. *Dissolve in a little HCl, add NH_4OH and $HC_2H_3O_2$ and test with H_2S.* White precipitate: ZnS. (15)

Filtrate: CrO_4^{--}. *Add $H_2C_2H_3O_2$ and Pb $(C_2H_3O_2)$.* Yello precip tate: $PbCrO_4$. (16)

* This precedure is that given by A. A. Noyes in his Qualitative Chemical Analysis, 8th edition, 1920.

PROCEDURE

METHOD B*

1. Boil a little of the filtrate from Group II until the hydrogen sulfide is expelled, pour into a mixture of 5 cc. 6-normal nitric acid and 5 cc. of ammonium molybdate reagent, heat to 60° and allow to stand for 10 minutes. If a yellow precipitate of ammonium phosphomolybdate is obtained, members of Group IV are likely to precipitate as phosphates upon the neutralization of the solution by ammonia and ammonium sulfide. The procedure in that case is modified as outlined in § 6.

Boil the remainder of the filtrate from Group II until hydrogen sulfide is expelled and make alkaline with ammonium hydroxide. (No precipitate shows absence of Al, Cr, Fe and alkaline-earth phosphate.) Add ammonium sulfide reagent in small portions until, after shaking the flask and blowing away the vapors, a black test is obtained with moist lead acetate paper held near the mouth of the flask. Heat nearly to boiling, shake and let stand about 3 minutes. Filter, wash the precipitate with water containing 1 per cent ammonium sulfide and finally with pure water. If the filtration is slow, keep the funnel covered with a watch glass to avoid oxidation of the precipitate. Test the filtrate with a few drops of ammonium sulfide reagent and heat to see if any dark precipitate forms which should be filtered off through a fresh filter. Use the filtrate for the Group IV tests (p. 118 or 120).

2. Digest the precipitate with 5–15 cc. of cold, 6-normal hydrochloric acid for a few minutes and afterwards boil for a short time. If there is a black residue, sprinkle a little powdered potassium chlorate into the hot, but not boiling, solution. Then boil for a minute and filter. Reject the residue, which should be sulfur possibly blackened by a little enclosed sulfide. Evaporate the solution nearly to dryness to remove the excess of acid, dilute to about 25 cc. and carefully neutralize with pure sodium hydroxide. If a very heavy precipitate is produced, it is best to dilute with a little more water. To the cold solution carefully add a little sodium peroxide powder. (On account of the violent reaction with water, and the fact that the powder often contains a little free sodium, care should be taken not to add the peroxide too fast or to a hot solution. Only a little peroxide should be taken from the container at one time and it should be transferred directly to glass and never to paper.) Finally boil the solution to decompose the excess of peroxide, dilute with an equal volume of water and filter. *The precipitate contains ferric hydroxide, hydrated manganese dioxide, cobaltic hydroxide and nickelous hydroxide. The filtrate contains sodium aluminate, chromate and zincate.* The separation is faulty in the case of zinc which normally stays in solution. As much as 5 mgs. of zinc may be carried down with the precipitate when much iron, nickel or cobalt is present, and as much as 20 mgs. by considerable manganese. This is probably due to the amphoteric nature of the precipitated hydroxides and the insolubility of the zinc salts of the corresponding acids. Examine the filtrate for chromium, aluminium and zinc by § 12.

3. Dissolve the precipitate in hot, 6-normal nitric acid, adding as much hydrogen peroxide as is necessary to reduce the manganese and cobalt to the bivalent condition (cf. p. 33). Evaporate the solution nearly to dryness, add 15 cc. of 16-normal nitric acid, about 1 gm. powdered potassium chlorate and heat to boiling. Add 10 cc. more of concentrated nitric acid, heat to boiling, remove the flame and add 0.5 gm. more of potassium chlorate. Repeat the treatment with fresh portions of chlorate until about 3 gms. of chlorate have been used. Do not add the chlorate to the nitric acid solution while it is boiling, as an explosion is likely to result, but boil after the addition of each portion of chlorate. The treat-

ment with chlorate is best accomplished in a 250-cc. Erlenmeyer flask. If a precipitate of MnO_2 is formed, filter through a thin layer of good-quality, washed asbestos which is supported by a little glass wool in an ordinary funnel. Test the filtrate for manganese by adding 1 gm. of potassium chlorate and boiling again. Wash the precipitate with a little concentrated nitric acid, which has been freed from nitrous acid by boiling with a little potassium chlorate just previous to use. Examine the filtrate for iron, cobalt, nickel and zinc by § 5.

4. Dissolve the precipitated manganese dioxide with a little hot 6-normal nitric acid and a few drops of hydrogen peroxide. Boil to decompose any excess of the latter and cool to room temperature. Add a little solid sodium bismuthate, shake and let the solid settle. A purple solution shows the presence of *manganese* (cf. p. 175).

5. In case phosphate is absent, pour the cold filtrate from (3) into a volume of 6-normal ammonium hydroxide which is four times as large as the volume of concentrated nitric acid used in (3). A dark red precipitate indicates the presence of iron. Filter and examine the filtrate for nickel, cobalt and zinc by § 7. Pour a mixture of 2 cc. potassium ferrocyanide reagent and 10 drops of 6-normal acetic acid over the precipitate of ferric hydroxide on the filter. A dark blue or green residue on the filter proves that *iron* is present.

6. In case a test for phosphoric acid was obtained in (1) first, test for iron as follows: Evaporate one-tenth of the solution from (3) almost to dryness, heat with 3 cc. of 6-normal hydrochloric acid till no more chlorine is evolved, and add 20 cc. of water with a little potassium ferrocyanide solution. If iron is present a dark blue color is obtained.

Neutralize the remainder of the nitric acid solution from (3) with ammonium hydroxide, adding the reagent until a slight precipitate is formed which does not redissolve by shaking for 15 seconds. In case no precipitate forms, add ammonium hydroxide until alkaline and pass on to § 7. If a precipitate forms, add 50 cc. of water and 15 cc. of 3-normal ammonium acetate solution. Unless the solution is already reddish in color, add ferric nitrate solution, in portions of 1 cc., until a deep red color is obtained. Boil the mixture gently for 3 minutes, adding 50 cc. more of water if a large precipitate form. (If the iron does not precipitate but remains in colloidal solution, add 30 drops more of ammonium hydroxide and boil again.) Filter while still hot and reject the precipitate. Make the filtrate alkaline with ammonium hydroxide, filter if necessary and treat the filtrate by § 7.

7. Saturate the filtrate from (5) with hydrogen sulfide, filter off the precipitated cobalt, nickel and zinc sulfides and reject the filtrate unless phosphate was found present and the procedure described in (6) was followed. In that case examine the filtrate for barium, calcium, strontium and magnesium but not for the alkalies, as these have been added. Digest the precipitated sulfides with 10–30 cc. of cold, normal hydrochloric acid to dissolve any zinc sulfide that may be present; a little nickel and a trace of cobalt may be dissolved by this treatment. Examine the solution for zinc by § 9 and § 11.

8. Test the sulfide residue obtained in (7) together with the sodium peroxide precipitate obtained in (9) for nickel and cobalt as follows: Dissolve the precipitate in a casserole by adding 5–15 cc. of 6-normal hydrochloric acid, heating to boiling and sprinkling a little potassium chlorate powder into the hot solution. Filter off any sulfur residue and evaporate the solution to dryness, but avoid overheating the residue. Dissolve in 5 cc. of 6-normal acetic acid, add 3 cc. of 6-normal potassium nitrite reagent and allow to stand with occasional shaking for at least 15 minutes.

A yellow precipitate of potassium cobaltinitrite proves *cobalt* to be present. If much precipitate forms, add to the mixture 10 cc. more of 6-normal potassium nitrite solution and about 3 grams of powdered potassium chloride. After standing with frequent shaking for another fifteen minutes, filter and reject the precipitate.

To a part of the filtrate, add 10 cc. of water and 4 cc. of dimethylglyoxime reagent. Heat to boiling and allow to stand for a few minutes. A red precipitate shows that *nickel* is present.

9. Neutralize the solution obtained in (7) with sodium hydroxide and add sodium peroxide as in (2). Examine the filtrate by § 11.

10. If deemed advisable, any precipitated $Ni(OH)_2$ and $Co(OH)_3$ from (9) may be added to the sulfide residue obtained in (7) and tested for nickel and cobalt as in (8).

11. Acidify the filtrate from (9) with acetic acid and saturate the solution with hydrogen sulfide. Any precipitate that forms is probably zinc sulfide. Confirm the *zinc* test as in Method A.

12. Acidify the filtrate from (3) with hydrochloric acid added in 2 cc. portions, cooling after each addition, and add ammonia until present in slight excess. Heat to boiling to coagulate any precipitated aluminium hydroxide and filter. Filter and examine the filtrate for chromium and zinc by § 14 and test the precipitate for aluminium by § 13.

13. Dissolve the aluminium hydroxide precipitate, or a part of it, in 5 cc. of 2-normal nitric acid. Add 5–10 cc. of water 2–15 cc. of 0.3-normal cobalt nitrate solution according to the probable aluminium content (cf. Method A, § 10), and 3 cc. of 6-normal ammonium hydroxide. Heat to boiling, filter and examine the filtrate by § 14. With the aid of suction, dry the precipitate as much as possible. Open the filter, tear off the paper that has no precipitate adhering to it and make a small roll of the remainder. Wind a platinum wire about this roll of paper and precipitate and heat in a flame until the carbon of the paper is all consumed. Finally ignite for a minute or two at a bright red heat. A blue residue shows that *aluminium* is present.

14. To the first filtrate obtained in (13) add 15 cc. of 3-normal sodium carbonate solution and evaporate in a porcelain casserole until no more vapors of ammonia are evolved. Then, if zinc is present, a white precipitate of basic zinc carbonate will appear. Filter and wash with hot water. Examine the precipitate by § 15 and the filtrate by § 16.

15. Dissolve the precipitate obtained in (14) by means of 10 cc. of hot 3-normal hydrochloric acid. Make the solution ammoniacal and add 3 cc. of 6-normal ammonium hydroxide in excess. If much zinc is present it will precipitate at the neutral point but redissolve in the excess of ammonia. If any precipitate remains of $Al(OH)_3$, $Cr(OH)_3$ or H_2SiO_3, filter it off and discard it. Make the solution slightly acid with acetic acid and saturate with hydrogen sulfide. A white precipitate of zinc sulfide shows the presence of *zinc*.

16. To the filtrate from (14), add acetic acid to acid reaction and 20 cc. of water, heat to boiling and add a little lead acetate solution. A yellow precipitate of lead chromate is formed if *chromium* is present. A white precipitate of lead chloride will usually form on cooling and has no significance.

METALS OF GROUP II. HYDROGEN SULFIDE GROUP

MERCURY, LEAD, COPPER, BISMUTH, CADMIUM, ARSENIC, ANTIMONY, TIN (GOLD, PLATINUM)

MERCURY, Hg. At. Wt. 200.6

Sp. Gr. = 13.6. M. Pt. = −38.7°. B. Pt. = 357°

Occurrence. — Mercury occurs in nature chiefly in the form of rhombohedral cinnabar, HgS; from the ore, free mercury is obtained by sublimation. According to G. F. Becker,* cinnabar is deposited from solutions of its thio salt. The richest deposits are those of New Almaden in California, where it occurs with serpentine, of Almaden in Spain, Idria in Carniola, and Moschellandsberg in the Palatinate of the Rhine. With cinnabar small quantities of native mercury are often found. Mercury is also an important constituent of many varieties of tetrahedrite.

Metallic mercury is the only one of the metals which is liquid at ordinary temperatures. It is insoluble in hydrochloric and dilute sulfuric acids, but is soluble in hot concentrated sulfuric acid with evolution of sulfur dioxide, forming mercurous or mercuric sulfate according to whether the metal or the acid is present in excess:

$$\mathrm{Hg} + 2\,\mathrm{H_2SO_4} = \mathrm{HgSO_4} + 2\,\mathrm{H_2O} + \mathrm{SO_2}\uparrow$$

$$2\,\mathrm{Hg} + 2\,\mathrm{H_2SO_4} = \mathrm{Hg_2SO_4} + 2\,\mathrm{H_2O} + \mathrm{SO_2}\uparrow .$$

Hydrobromic acid hardly attacks the metal at all, but hydriodic acid dissolves it readily with evolution of hydrogen:

$$\mathrm{Hg} + 4\,\mathrm{HI} = \mathrm{H_2[HgI_4]} + \mathrm{H_2}\uparrow .$$

The position of mercury in the electromotive series (p. 41) shows that mercury cannot be oxidized by H^+ except when the concentration of Hg^{++} is extremely low. This explains why mercury does not dissolve in dilute hydrochloric or sulfuric acid. It seems remarkable, therefore, that mercury should be oxidized by hydriodic acid. The reason the hydrogen of hydriodic acid can accomplish the oxidation of the mercury is because the compound $H_2[HgI_4]$ is scarcely dissociated at all into Hg^{++} ions (cf. p. 10).

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* Geology of the Quicksilver Deposits of the Pacific Slope. Washington, 1888.

The proper solvent for mercury is nitric acid.

If the metal is treated with hot, concentrated nitric acid, mercuric nitrate is formed:

$$\mathbf{Hg} + 4\,HNO_3 = Hg(NO_3)_2 + 2\,H_2O + 2\,NO_2\uparrow.$$

If, however, cold nitric acid is allowed to act upon an excess of mercury in the cold, mercurous nitrate is obtained:

$$Hg(NO_3)_2 + \mathbf{Hg} = Hg_2(NO_3)_2.$$

Mercury is attacked by chlorine, forming calomel (mercurous chloride):

$$2\,\mathbf{Hg} + Cl_2 = \mathbf{Hg_2Cl_2}.$$

Two oxides of mercury are known: yellow or red mercuric oxide, HgO; black mercurous oxide, Hg_2O.

These oxides are basic anhydrides, from which two series of salts are derived: (*a*) The mercuric salts, which contain Hg^{++}, and (*b*) the mercurous salts, which contain the group Hg_2^{++}. We will consider first the more stable mercuric salts.

Mercuric Salts

Mercuric salts are mostly colorless. The iodide is red or yellow. By heating the red, tetragonal crystals of mercuric iodide a yellow sublimate of orthorhombic needles is obtained, which gradually changes back to the red tetragonal modification. If the yellow crystals are rubbed the change takes place almost instantly. It is a general property of dimorphous bodies that *the more symmetrical form is almost always the more stable.*

The sulfide is black or red.

Mercuric chloride is soluble in water, 100 cc. of water dissolving 6.57 gm. at 10°, 7.39 gm. at 20°, 11.34 gm. at 50°, 24.3 gm. at 80° and 53.96 gm. at 100°.

In water containing hydrochloric acid, mercuric chloride is much more soluble than in pure water; and in fact the solubility increases with the concentration of the hydrochloric acid, due to the formation of the complex acid $H_2[HgCl_4]$. Alkali chlorides also help to dissolve mercuric chloride, forming salts of this complex acid. Mercuric chloride is more soluble in alcohol and in ether than it is in water.

The aqueous solution of mercuric chloride is a poor conductor of electricity; it is dissociated only to a slight extent and acts quite differently in many cases from a solution of the nitrate, which is a good conductor of electricity and contains, therefore, many mercuric ions. The cyanide differs from the nitrate even more, as we shall see.

Mercuric bromide is difficultly soluble in water (94 cc. of water at 9° dissolve only 1 gm. of the bromide), but is readily soluble in alcohol, and still more so in ether. The iodide is more difficultly soluble.

The halogen compounds of mercury readily form complex compounds with the halogen compounds of the alkalies, which are very stable.

Mercuric compounds are characterized furthermore by the readiness with which they undergo hydrolysis, forming insoluble basic salts. Thus the sulfate is decomposed when diluted largely with water (particularly on warming) into a yellow insoluble basic salt:

$$3\,HgSO_4 + 2\,H_2O \rightarrow 2\,H_2SO_4 + \mathbf{Hg_3O_2SO_4}.$$

Hydrogen ions prevent this hydrolysis.

The nitrate also is readily hydrolyzed into more or less insoluble basic salts, according to the dilution

$$Hg(NO_3)_2 + H_2O \rightleftarrows HNO_3 + \mathbf{Hg(OH)NO_3},$$

or

$$2\,Hg(NO_3)_2 + 2\,H_2O \rightleftarrows \mathbf{Hg_2O(OH)NO_3} + 3\,HNO_3.$$

The soluble salts of mercury are all poisonous. The chloride is easily volatilized and on evaporating a hydrochloric acid solution considerable mercuric chloride escapes with the water vapor.

Reactions in the Wet Way

A solution of mercuric chloride and one of mercuric nitrate are used for these reactions.

1. **Potassium Hydroxide** or **Sodium Hydroxide** precipitates yellow mercuric oxide:

$$HgCl_2 + 2\,OH^- \rightarrow 2\,Cl^- + H_2O + \mathbf{HgO}.$$

The hydroxides of the noble metals are exceedingly unstable; they lose water, as a rule, even in aqueous solution, forming the anhydrous oxide.

On adding a lesser amount of caustic potash to a solution of mercuric chloride, a reddish-brown precipitate of basic chloride is obtained:

$$2\,HgCl_2 + 2\,OH^- \rightarrow 2\,Cl^- + H_2O + \mathbf{Hg_2OCl_2},$$

or

$$3\,HgCl_2 + 4\,OH^- \rightarrow 4\,Cl^- + 2\,H_2O + \mathbf{Hg_3O_2Cl_2}.$$

In the presence of ammonium chloride, the precipitate formed by caustic alkalies is neither yellow nor red, but white as when ammonium hydroxide is added.

Mercuric oxide and the basic salts are readily soluble in acids.

2. **Ammonia** produces in a solution of mercuric chloride a white precipitate of mercuric aminochloride:

$$HgCl_2 + 2\,NH_3 \rightarrow NH_4^+ + Cl^- + \mathbf{Hg(NH_2)Cl}.$$

This compound, the so-called "infusible precipitate," volatilizes before it melts. It is soluble in acids, and in hot ammonium chloride, forming the "fusible precipitate":

$$\mathbf{Hg(NH_2)Cl} + NH_4Cl = Hg(NH_3)_2Cl_2.$$

If ammonia is allowed to act upon mercuric nitrate a white oxyamino compound is always formed:

$$2\,Hg(NO_3)_2 + 4\,NH_3 + H_2O \rightarrow 3\,NH_4NO_3 + O\begin{matrix}\diagup\,\mathbf{Hg}\,\diagdown\\ \diagdown\,\mathbf{Hg}\,\diagup\end{matrix}\mathbf{NH_2 \cdot NO_3}.$$

3. **Potassium Iodide** produces a red precipitate of mercuric iodide,

$$HgCl_2 + 2\,I^- \rightarrow 2\,Cl^- + \mathbf{HgI_2},$$

soluble in excess iodide ions, forming a colorless complex anion:

$$\mathbf{HgI_2} + 2\,I^- \rightarrow [HgI_4]^{--}.$$

This complex anion is scarcely dissociated at all into simple mercuric cations, for the solution gives no precipitate with caustic soda or potash. The alkaline solution is the so-called "Nessler's reagent," and serves for the detection of very slight traces of ammonia. There is formed in this reaction the brown-colored compound, $O\begin{matrix}\diagup\,Hg\,\diagdown\\ \diagdown\,Hg\,\diagup\end{matrix}NH_2 \cdot I$, which is soluble in an excess of the "Nessler's reagent," with an intense yellow color (cf. p. 94). Small quantities of mercury can also be detected by means of this reaction, in which case caustic alkali and ammonia are added to the solution which has been tested with potassium iodide.

4. **Alkali Carbonates** precipitate from both the chloride and the nitrate a reddish-brown basic carbonate in the cold,

$$4\,HgCl_2 + 4\,Na_2CO_3 = 8\,NaCl + 3\,CO_2\uparrow + \mathbf{Hg_4O_3 \cdot CO_3},$$

which on boiling loses carbon dioxide and is changed into yellow mercuric oxide.

5. **Alkali Bicarbonates** produce no precipitation in a solution of mercuric chloride, but do cause precipitation from mercuric nitrate:

$$4\,Hg(NO_3)_2 + 8\,NaHCO_3 = 8\,NaNO_3 + 4\,H_2O + 7\,CO_2\uparrow + \mathbf{Hg_4O_3CO_3}.$$

6. **Hydrogen Sulfide** produces in solutions of mercuric salts a precipitate which is at first white, then yellow, brown, and finally black. The white precipitate is formed according to the following equation:

$$3\,HgCl_2 + 2\,H_2S \rightarrow 4\,HCl + \mathbf{Hg_3Cl_2S_2}.$$

By the further action of hydrogen sulfide, black mercuric sulfide is finally obtained:

$$Hg_3Cl_2S_2 + H_2S = 2\,HCl + 3\,HgS.$$

Mercuric sulfide is insoluble in dilute boiling acids. Hot concentrated nitric acid transforms it gradually into white $Hg_3S_2(NO_3)_2$,

$$9\,HgS + 8\,HNO_3 = 2\,NO\uparrow + 3\,S + 4\,H_2O + 3\,Hg_3S_2(NO_3)_2,$$

which by long boiling is changed into the soluble nitrate.

It dissolves readily in aqua regia, forming the chloride with separation of sulfur:

$$3\,HgS + 6\,HCl + 2\,HNO_3 = 3\,HgCl_2 + 3\,S + 2\,NO\uparrow + 4\,H_2O.$$

Mercuric sulfide is insoluble in caustic soda and potash solutions, and in ammonium sulfide, but it dissolves readily in sodium or potassium sulfide:

$$HgS + K_2S = Hg(SK)_2.$$

By dilution with water this compound is completely hydrolyzed into mercuric sulfide, potassium hydrosulfide and potassium hydroxide:

$$Hg(SK)_2 + H_2O \rightleftarrows KOH + KSH + HgS.$$

Therefore it is always necessary to dissolve the mercuric sulfide with considerable potassium sulfide, or with little potassium sulfide and considerable caustic potash, in order to prevent this hydrolysis.

The fact that $Hg(SK)_2$ is so readily hydrolyzed explains the formation of cinnabar in nature. In the interior of the earth the thio compound is formed, which is brought by springs to the surface and there undergoes the above decomposition.

Ammonium chloride precipitates mercuric sulfide from its solution in alkaline sulfide. Unlike the sulfide of silver, lead, bismuth and cadmium, mercuric sulfide is soluble in potassium thiocarbonate solution, and unlike palladium, it is precipitated from such a solution by means of carbon dioxide gas.

7. **Potassium Cyanide** produces in a solution of mercuric chloride no precipitation, because the cyanide, as well as the chloride, forms readily soluble complex compounds with alkali chlorides. The following are known: $K[HgCl_3]$, $K_2[HgCl_4]$, $K[Hg(CN)_2Cl]$, $K_2[Hg(CN)_2Cl_2]$ and $K_2[Hg(CN)_4]$.

In a concentrated solution of mercuric nitrate, potassium cyanide produces a precipitate of mercuric cyanide, soluble in considerable water and in potassium cyanide:

$$Hg(NO_3)_2 + 2\,CN^- \rightarrow 2\,NO_3^- + Hg(CN)_2.$$

Mercuric cyanide is the only cyanide of the heavy metals that is soluble in water. It dissolves mercuric oxide perceptibly, forming

the complex compound $(HgCN)_2O$. Mercuric cyanide is not precipitated by alkali carbonates or by caustic alkalies, because mercuric oxide is soluble in mercuric cyanide. It is not decomposed by dilute sulfuric acid, although it is by the halogen acids — most difficultly by hydrochloric acid, and most readily by hydriodic acid; hydrogen sulfide decomposes it with precipitation of mercuric sulfide:

$$Hg(CN)_2 + H_2S = 2\,HCN + \mathbf{HgS}.$$

8. **Neutral Alkali Chromates** precipitate yellow mercuric chromate from both the chloride and nitrate solutions. On long standing or by boiling, the precipitate becomes red, a basic salt being probably formed.

9. **Alkali Dichromates** throw down a yellowish-brown precipitate from the nitrate solution, but not from the chloride.

10. **Ferrous Sulfate** reduces mercuric nitrate on boiling to metallic mercury:

$$Hg(NO_3)_2 + 2\,Fe^{++} \rightarrow 2\,Fe^{+++} + 2\,NO_3^- + \mathbf{Hg}.$$

Mercuric chloride and cyanide are not reduced by ferrous sulfate.

11. **Stannous Chloride** reduces mercuric salts, first to insoluble mercurous chloride (calomel),

$$2\,HgCl_2 + Sn^{++} \rightarrow Sn^{++++} + \mathbf{Hg_2Cl_2} + 2\,Cl^-,$$

and by further action to free mercury,

$$\mathbf{Hg_2Cl_2} + Sn^{++} = Sn^{++++} + 2\,\mathbf{Hg} + 2\,Cl^-.$$

Metallic mercury separates out in the form of a gray powder. By decanting the solution, and boiling the residue with dilute hydrochloric acid, the mercury appears in tiny globules.

12. **Copper, Zinc,** and **Iron** precipitate mercury from solutions of its salts:

$$HgCl_2 + \mathbf{Fe} = Fe^{++} + 2\,Cl^- + \mathbf{Hg},*$$

$$HgCl_2 + 2\,\mathbf{Cu} = \mathbf{Cu_2Cl_2} + \mathbf{Hg}.$$

On placing a drop of mercury solution (whether of a mercurous or a mercuric salt) upon a piece of bright copper-foil, a gray spot is formed, which, when dry, becomes as bright as silver by rubbing.

13. **Ammonium Thioacetate** added to a cold solution of mercuric salt containing hydrochloric acid produces a white precipitate of mercuric sulfochloride but, in a hot solution, black mercuric sulfide is formed.

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* This reaction is employed for detecting metallic iron in the presence of FeO. If an excess of $HgCl_2$ is present Hg_2Cl_2 is formed (cf. p. 156).

14. **Sodium Thiosulfate** produces in a boiling-hot, acid solution a precipitate which is at first white, then orange-yellow, and finally black. The precipitated sulfur, however, is likely to conceal a small quantity of the mercury precipitate.

Mercurous Salts

Mercurous salts all contain the bivalent mercurous group Hg_2^{++} and are changed more or less readily into mercuric salts, splitting off one atom of mercury from the molecule. Mercurous salts containing oxygen, like mercuric salts, are readily hydrolyzed in dilute aqueous solutions; thus the nitrate is decomposed according to the equation

$$Hg_2(NO_3)_2 + HOH = HNO_3 + \mathbf{Hg_2(OH)NO_3}.$$

Mercurous chloride (calomel) is insoluble in water and hydrochloric acid, but soluble in nitric acid and aqua regia.

Reactions in the Wet Way

1. **Caustic Potash** precipitates black mercurous oxide:

$$Hg_2(NO_3)_2 + 2\,OH^- \rightarrow 2\,NO_3^- + H_2O + \mathbf{Hg_2O}.$$

2. **Ammonia** produces a black precipitate of mercuric amino salt mixed with metallic mercury:

$$2\,Hg_2(NO_3)_2 + 4\,NH_3 + H_2O = 3\,NH_4NO_3 + O\begin{matrix}\diagup\,\mathbf{Hg}\,\diagdown\\ \diagdown\,\mathbf{Hg}\,\diagup\end{matrix}\mathbf{NH_2NO_3} + 2\,\mathbf{Hg}.$$

It can easily be shown that this precipitate contains metallic mercury by rubbing a piece of pure gold over it; silver-lustrous gold amalgam will be formed.

Mercurous chloride gives with ammonia a mercuric amine with separation of metallic mercury:

$$\mathbf{Hg_2Cl_2} + 2\,NH_3 = NH_4Cl + \mathbf{Hg(NH_2)Cl} + \mathbf{Hg}.$$

By boiling the black precipitate with dilute hydrochloric acid or with concentrated ammonium chloride solution, the mercuric amine goes into solution, leaving behind drops of mercury.

3. **Alkali Carbonates** give, first, a yellow precipitation of the carbonate, which quickly becomes gray, owing to the formation of mercuric oxide, metallic mercury, and carbon dioxide:

$$Hg_2(NO_3)_2 + Na_2CO_3 = 2\,NaNO_3 + \mathbf{Hg_2CO_3},$$

and

$$\mathbf{Hg_2CO_3} = \mathbf{HgO} + \mathbf{Hg} + CO_2\uparrow.$$

4. **Ammonium Carbonate** yields the same precipitate as ammonia.

5. **Hydrogen Sulfide** immediately throws down a black precipitate of mercuric sulfide and mercury (difference from mercuric salts):

$$Hg_2(NO_3)_2 + H_2S = 2\,HNO_3 + \mathbf{HgS} + \mathbf{Hg}.$$

The black precipitate does not dissolve completely in potassium sulfide, the mercury remaining insoluble, but in alkali polysulfides the entire precipitate dissolves.

From such a solution, ammonium chloride throws down black mercuric sulfide.

6. **Hydrochloric Acid** and **Soluble Chlorides** precipitate white mercurous chloride (calomel),

$$Hg_2(NO_3)_2 + 2\,Cl^- \rightarrow 2\,NO_3^- + \mathbf{Hg_2Cl_2},$$

insoluble in water and dilute acids, soluble in strong nitric acid and aqua regia. Oh boiling for a long time with water, calomel becomes gray, owing to a partial decomposition into mercuric chloride and mercury.

On boiling with concentrated sulfuric acid, mercuric sulfate is formed with evolution of sulfur dioxide and hydrogen chloride:

$$(a)\ \mathbf{Hg_2Cl_2} + H_2SO_4 = 2\,HCl\uparrow + Hg_2SO_4.$$

$$(b)\ Hg_2SO_4 + 2\,H_2SO_4 = 2\,H_2O + SO_2\uparrow + 2\,HgSO_4.$$

7. **Neutral Potassium Chromate** precipitates red mercurous chromate on boiling (cf. p. 149):

$$Hg_2(NO_3)_2 + K_2CrO_4 = 2\,KNO_3 + \mathbf{Hg_2CrO_4}.$$

8. **Potassium Iodide** precipitates green mercurous iodide,

$$Hg_2(NO_3)_2 + 2\,KI = 2\,KNO_3 + \mathbf{Hg_2I_2},$$

partly soluble in an excess of the precipitant, with the formation of potassium mercuric iodide and the separation of mercury:

$$\mathbf{Hg_2I_2} + 2\,I^- \rightarrow [HgI_4]^{--} + \mathbf{Hg}.$$

9. **Potassium Cyanide** precipitates metallic mercury, mercuric cyanide being formed at the same time:

$$Hg_2(NO_3)_2 + 2\,KCN = 2\,KNO_3 + \mathbf{Hg(CN)_2} + \mathbf{Hg}.$$

10. **Stannous Chloride** added in very small quantities precipitates white mercurous chloride, but if more than an equivalent weight of stannous ions is added, a gray mixture of mercurous chloride and finely-divided mercury is obtained, and eventually all of the mercurous chloride can be changed to free mercury.

$$Hg_2(NO_3)_2 + Sn^{++} \rightarrow Sn^{++++} + 2\,NO_3^- + \mathbf{2\,Hg}.$$

11. **Ammonium Thioacetate** and **Sodium Thiosulfate** produce sulfide precipitates when added to acid solutions of mercurous salts, the precipitates consisting of black mercuric sulfide and finely-divided mercury together with sulfur.

12. **Polished Copper** touched with a drop of nearly neutral mercurous solution causes the deposition of metallic mercury. If, after a short time, the solution is washed off and the copper is rubbed gently with a woolen cloth or piece of paper, a silver-white, lustrous spot is obtained.

Reactions of Mercury in the Dry Way

Nearly all mercury compounds sublime on being heated in the closed tube. Mercuric chloride first melts, then vaporizes, forming a crystalline deposit on the cold sides of the tube. Mercurous chloride sublimes; the sublimate is almost white, but there is a slight grayish tint owing to the decomposition of a small part of the substance into mercuric chloride and mercury. Mercuric iodide yields a yellow sublimate, which becomes red on being rubbed with a glass rod. Mercury compounds containing oxygen (all more or less unstable) yield mercury.

The sulfide gives a black sublimate.

All compounds of mercury, when mixed with sodium carbonate and heated in a closed tube, yield a gray mirror, consisting of small globules of mercury. In order to make the drops more apparent, place a piece of filter-paper over a glass rod, and rub the mirror with it. The small drops then run together into large ones, stick to the paper, and can be removed from the glass.

*Detection of Mercury in Urine**

Treat 500 to 1000 cc. of urine in a beaker with 0.5 per cent hydrochloric or sulfuric acid, add 0.5 gm. of brass wool (such as is used for the ornamentation of Christmas trees) and, while heating on the water-bath to 60° or 80°, pass air through the liquid for from ten to fifteen minutes, to keep it in constant motion. Any mercury present is replaced by copper: $HgCl_2 + Cu = CuCl_2 + Hg$.

The mercury, as fast as it is set free, amalgamates with the excess of copper present. Pour off the liquid from the tiny threads of brass and wash thoroughly by decantation with distilled water, then with alcohol, and finally with ether. Press the brass thread between layers of filter-paper, to free them from any adhering ether, and roll them between the fingers into a small pellet. Introduce this pellet into a thoroughly cleansed and perfectly dry glass tube, 10 cm. long, 0.5 cm. wide and closed at one end. With the aid of the blast flame, draw out a capillary of about 1 mm. width in the tube about 0.5 cm. away from the brass, toward the open end of the tube. After cooling the tube, heat the bottom of it, in which the sample

* P. FÜBRINGER, *Z. anal. Chem.*, **27**, 526 (1888).

rests, to dark redness. This causes the mercury to distill off and it is condensed in the colder portion of the tube in a gray mirror consisting of tiny drops. If any considerable amount of mercury is present, e.g., more than 1 mg., the drops of mercury can be distinctly seen with a lens. If less than 1 mg. of mercury is present in the urine, it is very difficult to distinguish the mirror. In this case to make it perceptible, transform the mercury into scarlet-red mercuric iodide. To accomplish this, place a small crystal or two of iodine in a test-tube and cut off the tube containing the mercury mirror just above the place where the ball of brass rests and place the part of the tube containing the mercury in the test-tube. Cautiously heat the bottom of the test-tube over a gas flame. As soon as the violet vapors of iodine reach the place where the mercury was deposited, the latter is transformed, by very gentle heating, into the red iodide, which can be seen most distinctly by removing the little tube and laying it upon a piece of white paper. This method is very sensitive and permits the positive recognition of as little as 0.4 mg. of $HgCl_2$.*

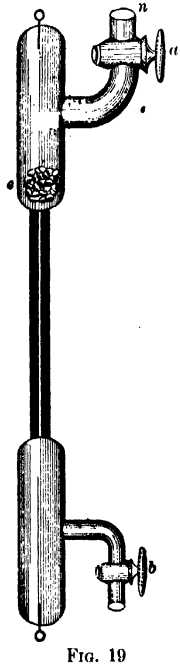


FIG. 19

Detection of Mercury Vapors in the Air

Place a piece of pure gold leaf in a small glass tube and draw the air to be tested through the tube for an hour, at a rate not greater than one liter per minute. Meanwhile evacuate a Geissler tube, of the form shown in Fig. 19, by means of a water pump (not a mercury pump!) and finally close both stopcocks. Place the gold leaf, which now contains as amalgam any mercury that was present in the air tested, in the tube *n* and suddenly open the cock *a*, which has a wide bore; this causes the gold to be sucked into the tube, stopping at *c*, the mouth of the capillary opening. The next step is to replace the air in the tube by hydrogen. Introduce hydrogen gas, obtained from a Kipp generator and dried by concentrated sulfuric acid, at *a* and allow the gas to pass out at *b*. After a rapid stream of the gas has passed through the tube for three minutes, close the cocks *a* and *b*, without disconnecting the Kipp generator, connect *b* with the suction pump † and evacuate the apparatus for a minute or two; then close *b*, and open *a* (which causes more hydrogen to enter the apparatus); close *a* again, open *b* and once more evacuate the apparatus. Repeat this alternate introduction of hydrogen gas and evacuation five or six times. In this way the air is entirely replaced by hydrogen. Finally evacuate the tube for five or ten minutes and close the cock *b*. Place the capillary in front of the slit of a spectroscope and allow the secondary current of an induction apparatus to pass through the tube. In the presence of the merest trace of mercury, the charac-

* For other methods of detecting mercury in urine, see JOLLES, *Z. anal. Chem.*, **39**, 230 (1900); MERGET, *J. Pharm. Chim.* [5], **19**, 444 (1889); and OPPENHEIM, *Z. anal. Chem.*, **42** (1903), 431.

† Between the water suction-pump and the Geissler tube, a calcium chloride drying tube should be introduced.

teristic green line 546 $\mu\mu$ is distinctly visible in the cold, and with somewhat larger amounts of mercury the indigo-blue line at 456 $\mu\mu$ can be seen. If the wad of gold leaf is cautiously warmed with the Bunsen flame, the mercury spectrum appears still more sharply.

Remark. This test is so extremely sensitive that a blank test performed in places where work with mercury has been performed will often show the presence of this element in the atmosphere.

If the apparatus has been once used for the detection of mercury it must be thoroughly cleansed before it is used again for this purpose. To this end, remove the gold and allow aqua regia to remain in the tube for several minutes. Draw out the acid and rinse the tube three times with distilled water, once with absolute alcohol * and finally dry by passing dry hydrogen through the tube for five minutes, while warming it at the same time. Ignite the gold gently to distill off any mercury it may contain. If now on introducing the gold and evacuating the apparatus, the mercury spectrum is no longer visible, the tube is ready for a new experiment.

It may be mentioned that the two platinum wires in the Geissler tube must not be provided with aluminium points, because aluminium amalgamates with mercury, and when the points are once amalgamated it is impossible to free the tube sufficiently from mercury to permit its use for subsequent experiments.

LEAD, Pb. At. Wt. 207.20

Sp. Gr. = 11.36–11.39. M. Pt. = 327.4° B. Pt. = 1600°

Occurrence. — Galena, PbS, isometric; cerussite, $PbCO_3$, orthorhombic and isomorphous with aragonite, $CaCO_3$; anglesite, $PbSO_4$, orthorhombic, isomorphous with anhydrite, $CaSO_4$, celestite, $SrSO_4$, and barite, $BaSO_4$; pyromorphite, $Pb_5(PO_4)_3Cl$, hexagonal; mimetite, $Pb_5(AsO_4)_3Cl$; vanadinite, $Pb_5(VO_4)_3Cl$. The last three minerals are isomorphous and belong to the apatite group. Other minerals which may be mentioned are wulfenite, $PbMoO_4$, tetragonal, isomorphous with stolzite, $PbWO_4$, and the monoclinic crocoite, $PbCrO_4$.

Lead is a bluish-gray metal. It is attacked by all acids. As, however, most lead salts are difficultly soluble in water, it usually becomes coated with a layer of salt, which protects it from further action of the acid. Thus lead is immediately attacked by dilute sulfuric acid according to the equation

$$Pb + H_2SO_4 = PbSO_4 + H_2\uparrow .$$

But, as lead sulfate is insoluble in dilute sulfuric acid, the reaction quickly ceases. Upon this principle rests the use of "lead chambers" in the manufacture of sulfuric acid, and the use of "lead pans" for the concentration of the dilute "chamber acid." It has, however, been found from experience that the sulfuric acid should not be concentrated too much in lead pans — stopping when a 78–82 per cent acid

* All these operations must be carried out in a space where there are positively no mercury vapors present in the atmosphere.

is obtained. The protecting layer of lead sulfate is soluble in hot concentrated sulfuric acid, forming soluble lead bisulfate, $PbSO_4 + H_2SO_4 \rightarrow Pb(HSO_4)_2$, so that the hot concentrated acid can act on the freshly-exposed surface of lead:

$$Pb + 3\,H_2SO_4 \rightarrow 2\,H_2O + Pb(HSO_4)_2 + SO_2\uparrow.$$

Lead behaves quite similarly on treatment with hydrochloric acid. On the surface a protecting coating of lead chloride is obtained, which is soluble in hot concentrated hydrochloric acid, forming $H[PbCl_3]$. Lead is soluble, therefore, in concentrated hydrochloric acid.

$$Pb + 3\,HCl = H[PbCl_3] + H_2\uparrow.$$

Hydrofluoric acid attacks lead similarly, forming a protecting layer of lead fluoride, which is insoluble in hydrofluoric acid. Consequently lead retorts can be used for the distillation of hydrofluoric acid and in the preparation of hydrofluoric acid by means of fluorite and sulfuric acid.

Dilute nitric acid is the proper solvent for lead. Lead nitrate is insoluble in strong nitric acid, so that lead does not dissolve in concentrated nitric acid; the solution must be sufficiently dilute to prevent the separation of the lead nitrate formed.

Lead forms the following oxides: lead suboxide, Pb_2O; lead protoxide (litharge and massicot), PbO; lead sesquioxide, Pb_2O_3; minium (red lead), Pb_3O_4; and lead peroxide, PbO_2.

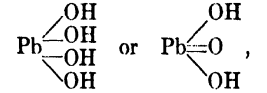
Of these oxides, PbO alone is the anhydride of a base;* from it the salts of lead are derived, in which the lead is bivalent. This lead protoxide (litharge) is a yellow powder, which melts at about 980° C., and solidifies on slow cooling, forming tetragonal crystals (needles). It is slightly soluble in water with an alkaline reaction, and is readily soluble in dilute nitric acid.

Lead suboxide, Pb_2O, is formed as a black velvety powder on heating the oxalate to about 300° C.:

$$2\,PbC_2O_4 = 3\,CO_2\uparrow + CO\uparrow + Pb_2O.$$

On heating the suboxide in the air, it becomes readily oxidized to lead protoxide.

Lead dioxide, PbO_2, may be regarded as the anhydride of orthoplumbic acid, H_4PbO_4, or metaplumbic acid, H_2PbO_3,



Orthoplumbic acid Metaplumbic acid

* Although $Pb(C_2H_3O_2)_4$ is known.

just as SiO_2, SnO_2, CO_2 and MnO_2, are anhydrides of silicic, stannic, carbonic, and manganous acids. The acid H_2PbO_3 is formed by the oxidation of lead hydroxide, $Pb(OH)_2$, in alkaline solution by means of hypochlorites, chlorine, bromine, hydrogen peroxide, or potassium persulfate:

$$\mathbf{Pb(OH)_2} + 2\,OH^- + Cl_2 \rightarrow H_2O + 2\,Cl^- + \mathbf{H_2PbO_3}.$$

The brown metaplumbic acid which separates out goes over at 100° C. into the anhydride; and the latter on ignition loses oxygen, changing into yellow lead protoxide. The other two oxides of lead, Pb_2O_3 and Pb_3O_4, may be regarded as salts of the plumbic acids; Pb_2O_3 as lead metaplumbate, $PbPbO_3$, and Pb_3O_4 as the lead orthoplumbate, Pb_2PbO_4.

Pb_2O_3 is obtained as a yellow precipitate on gently oxidizing an alkaline solution of lead monoxide by means of hypochlorites, halogens, hydrogen peroxide, or persulfates,

$$2\,Pb(OH)_2 + 2\,OH^- + Cl_2 \rightarrow 2\,Cl^- + 3\,H_2O + \mathbf{Pb_2O_3},$$

and the red minium, Pb_3O_4, by igniting lead oxide or lead carbonate for some time in the air at about 430° C.:

$$6\,\mathbf{PbO} + O_2 = 2\,\mathbf{Pb_3O_4}.$$

Both Pb_2O_3 and Pb_3O_4 behave chemically as salts; for, on treating with nitric acid, brown plumbic acid and lead nitrate are formed, which corresponds to the action of nitric acid on, say, lead carbonate:

$$\mathbf{PbPbO_3} + 2\,H^+ \rightarrow Pb^{++} + \mathbf{H_2PbO_3},$$
$$\mathbf{Pb_2PbO_4} + 4\,H^+ \rightarrow 2\,Pb^{++} + H_2O + \mathbf{H_2PbO_3}.$$

These salt-like oxides * are perfectly analogous to those of manganese; on treatment with hydrochloric acid they yield chlorine, the plumbic acid, at first set free, behaving like a peroxide:

$$\mathbf{PbO_2} + 4\,HCl = 2\,H_2O + PbCl_2 + Cl_2\uparrow;$$
$$\mathbf{Pb_2O_3} + 6\,HCl = 3\,H_2O + 2\,PbCl_2 + Cl_2\uparrow;$$
$$\mathbf{Pb_3O_4} + 8\,HCl = 4\,H_2O + 3\,PbCl_2 + Cl_2\uparrow.$$

Reactions in the Wet Way

Most lead salts are difficultly soluble or insoluble in water; but all dissolve in dilute nitric acid, excepting, perhaps, fused lead chromate, which is very difficultly soluble.

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* Besides the lead salts of plumbic acid, alkali and alkaline earth salts are known.

1. **Potassium** and **Sodium Hydroxides** precipitate white lead hydroxide,

$$Pb^{++} + 2\,OH^- \rightarrow \mathbf{Pb(OH)_2},$$

soluble in an excess of the precipitant, forming a plumbite:

$$\mathbf{Pb(OH)_2} + OH^- \rightarrow H_2O + HPbO_2^-.$$

$Pb(OH)_2$ is also slightly soluble in water which is free from carbonic acid. The aqueous solution of lead hydroxide is slightly alkaline. The addition of hydrogen peroxide, hypochlorite or persulfate causes precipitation of dark brown lead peroxide, PbO_2.

2. **Ammonia** precipitates the white hydroxide, insoluble in excess of the reagent.

3. **Alkali Carbonates** precipitate white basic lead carbonate. *Alkali bicarbonates* precipitate the normal carbonate.

4. **Sodium Phosphate** precipitates white lead phosphate,

$$3\,Pb^{++} + 4\,HPO_4^{--} \rightarrow 2\,H_2PO_4^- + \mathbf{Pb_3(PO_4)_2},$$

insoluble in acetic acid, readily soluble in nitric acid, caustic soda or potash.

5. **Potassium Cyanide** precipitates white lead cyanide, insoluble in an excess.

6. **Hydrochloric Acid** or **Soluble Chlorides** precipitate from moderately concentrated solutions, white flocculent lead chloride:

$$Pb^{++} + 2\,Cl^- \rightarrow \mathbf{PbCl_2},$$

difficultly soluble in cold water (135 parts of water dissolve 1 part of $PbCl_2$), but much more soluble in hot water; on cooling the solution, lead chloride separates in the form of glistening needles or plates. Lead chloride is much more soluble in concentrated hydrochloric acid and in a concentrated solution of a chloride of an alkali than it is in water, as it forms complex compounds with these substances such as $H[PbCl_3]$, $K[PbCl_3]$, which are, however, decomposed on dilution with water, with separation of lead chloride.

7. **Potassium Iodide** precipitates yellow lead iodide:

$$Pb^{++} + 2\,I^- \rightarrow \mathbf{PbI_2}.$$

The iodide is much less soluble in water than the chloride (195 cc. of boiling water dissolve only 1 gm. of lead iodide), forming a colorless solution from which lead iodide separates on cooling, in the form of golden yellow plates.

The iodide dissolves to a considerable extent in hydriodic acid, and in a solution of an alkali iodide, forming lead hydriodic acid, $H[PbI_3]$ or one of its salts (such as $K[PbI_3]$), all of which are decomposed on dilution, with deposition of lead iodide.

8. **Alkali Chromates** produce a yellow precipitate of lead chromate,

$$Pb^{++} + CrO_4^{--} \rightarrow \mathbf{PbCrO_4}$$

and

$$2\,Pb^{++} + Cr_2O_7^{--} + 2\,C_2H_3O_2^- + H_2O \rightarrow 2\,HC_2H_3O_2 + 2\,\mathbf{PbCrO_4}.$$

Lead chromate is insoluble in acetic acid, but soluble in nitric acid and in caustic alkali.

9. **Hydrogen Sulfide** produces in dilute lead solutions (from slightly acid solutions, as well as from neutral or alkaline ones) a black precipitate of lead sulfide:

$$Pb^{++} + H_2S \rightleftarrows 2\,H^+ + \mathbf{PbS}.$$

From hydrochloric acid solutions an orange-red precipitate of lead sulfochloride is at first obtained,

$$2\,PbCl_2 + H_2S \rightarrow 2\,HCl + \mathbf{Pb_2Cl_2S},$$

which is decomposed immediately by more hydrogen sulfide, forming the black lead sulfide. In this respect lead salts are similar to mercuric salts (see p. 210).

Lead sulfide is soluble in dilute, boiling, 2-normal nitric acid, forming lead nitrate, with separation of sulfur:

$$3\,\mathbf{PbS} + 2\,HNO_3 + 6\,H^+ \rightarrow 3\,Pb^{++} + 4\,H_2O + 2\,NO\uparrow + 3\,\mathbf{S}.$$

The reaction usually goes a little farther; some of the sulfur is oxidized to sulfuric acid, forming insoluble lead sulfate. The amount of sulfuric acid formed (and therefore of the lead sulfate also) increases with the concentration of the acid.

Lead sulfide is also soluble in strong hydrochloric acid:

$$\mathbf{PbS} + 2\,H^+ \rightleftarrows Pb^{++} + H_2S\uparrow.$$

10. **Ammonium Thioacetate** added to an acid solution of a lead salt produces at first a red precipitate of sulfochloride and finally a black precipitate of lead sulfide.

11. **Sodium Thiosulfate** produces a white precipitate of lead thiosulfate, soluble in an excess of the precipitant forming, as in the case of a silver salt, a complex thiosulfate ion. In the presence of acid, lead sulfide is precipitated on boiling.

12. **Sulfuric Acid** and **Soluble Sulfates** in solutions of lead salts cause the separation of white, difficultly soluble lead sulfate:

$$Pb^{++} + H_2SO_4 \rightarrow 2\,H^+ + \mathbf{PbSO_4}.$$

One part of the salt dissolves at the ordinary temperature in 22,800 cc. of water; in water containing a little sulfuric acid it is still less soluble, while in alcohol it is insoluble. Lead sulfate dissolves appreciably in hot, dilute hydrochloric or nitric acid, forming $Pb(HSO_4)_2$. On

cooling the hydrochloric acid solution, lead chloride separates out in needles. Almost all the sulfuric acid of commerce contains some dissolved lead sulfate. In order to detect this, 200–300 cc. of the concentrated acid should be diluted with an equal volume of water and allowed to stand twelve hours, whereby the lead sulfate separates as a white powder.

Besides being soluble in acids, lead sulfate is easily soluble in caustic alkalies, and in solutions containing the ammonium salts of many organic acids. This last property is of great importance for the analytical chemist, as it offers a means for separating lead sulfate from barium sulfate, silica, etc., which remain undissolved. Ammonium acetate or ammonium tartrate is usually used as the solvent.

The reason lead sulfate dissolves in a *concentrated* solution of ammonium acetate is due to the formation of lead acetate, which is ionized only to a very slight extent in the presence of an excess of acetate ions:

$$PbSO_4 + 2\,C_2H_3O_2^- \rightarrow Pb(C_2H_3O_2)_2 + SO_4^{--}.$$

Similarly, ammonium tartrate in aqueous solution dissolves lead sulfate by forming a tartrate which does not ionize to any extent into simple lead cations. Lead sulfate also dissolves easily in caustic alkali solutions, forming alkali plumbites.

From all these solutions the lead can be precipitated as chromate by the addition of potassium chromate, as sulfate upon the addition of dilute sulfuric acid or as sulfide by ammonium sulfide.

Reactions in the Dry Way

Heated with sodium carbonate on charcoal, all lead compounds yield a malleable button, surrounded with an incrustation of the yellow oxide. On the charcoal stick also, the malleable button is readily obtained.

Lead glass turns black on heating in the reducing flame, owing to the separation of lead.

BISMUTH, Bi. At. Wt. 208.0

Sp. Gr. = 9.8. M. Pt. = 270°. B. Pt. about 1435°

Occurrence. — Bismuth usually occurs native with nickel and cobalt ores. The following ores are of no great importance: Bismite, Bi_2O_3; bismuthinite, Bi_2S_3; emplectite, $Bi_2S_3Cu_2$; bismutite, $3\,[BiOH][CO_3] \cdot 5\,Bi(OH)_3$.

Bismuth is a brittle, reddish-white metal which crystallizes in the hexagonal system. The proper solvent for bismuth (as is the case

with most other metals) is nitric acid. Hydrochloric acid does not attack bismuth, and sulfuric acid dissolves it only on warming.

Bismuth forms three oxides: bismuth trioxide, Bi_2O_3, bismuth tetroxide, Bi_2O_4, and bismuth peroxide, Bi_2O_5.

Bismuth trioxide is a basic anhydride,* from which most bismuth salts are derived. Bismuth pentoxide, a brownish substance, acts as an acid anhydride, forming an acid, $HBiO_3$, corresponding to metaphosphoric acid. Salts of this acid have never been prepared in a pure state. On igniting, Bi_2O_5 loses oxygen, forming yellow Bi_2O_3. It dissolves in hydrochloric acid with evolution of chlorine, forming a salt of trivalent bismuth:

$$Bi_2O_5 + 10\,HCl = 5\,H_2O + 2\,BiCl_3 + 2\!\uparrow\!Cl_2\uparrow .$$

Bismuth tetroxide is a brown powder which is sometimes used as an efficient oxidizing agent. Commercial sodium bismuthate is probably a mixture of $NaBiO_3$ and Bi_2O_4.

Bismuth salts are mostly colorless, and are all insoluble in considerable water, on account of being hydrolyzed into an insoluble basic salt; thus the chloride is quantitatively decomposed into basic bismuth chloride, often called *bismuthyl chloride*,

$$BiCl_3 + H_2O \rightleftarrows 2\,HCl + \mathbf{BiOCl},$$

insoluble in tartaric acid (difference from antimony).

Bismuthyl chloride is readily soluble in hydrochloric acid, the above equation taking place from right to left. The reaction, therefore, is reversible and the relative amounts of water and hydrochloric acid present determine in which direction the reaction will go. On adding water to a slightly acid solution of $BiCl_3$, a white precipitate of the basic chloride appears immediately. On carefully adding hydrochloric acid, the precipitate again dissolves, but may be reprecipitated by the addition of more water. All the other compounds of bismuth act as the chloride. The nitrate yields, at first, an amorphous precipitate of $BiONO_3$,

$$Bi(NO_3)_3 + H_2O \rightleftarrows 2\,HNO_3 + \mathbf{BiO(NO_3)},$$

which becomes more basic and crystalline on further addition of water:

$$2\,\mathbf{BiO(NO_3)} + H_2O \rightleftarrows \mathbf{Bi_2O_2(OH)(NO_3)} + HNO_3.$$

This last compound is the *bismuth subnitrate* which is so much used in medicine.

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* Bismuth trioxide acts as a weak acid under some circumstances (cf. foot-note, p. 224).

Reactions in the Wet Way

1. **Potassium Hydroxide** precipitates, in the cold, white bismuth hydroxide,

$$Bi^{+++} + 3\,OH^- \rightarrow \mathbf{Bi(OH)_3},$$

which, on boiling, becomes pale yellow:

$$\mathbf{Bi(OH)_3} \rightarrow H_2O + \mathbf{BiO(OH)}.$$

Both of these hydroxides are insoluble in an excess of the precipitant,* but are readily soluble in acids.

On adding to the alkaline solution, in which the hydroxide is suspended, chlorine, bromine, hypochlorites, or hydrogen peroxide, the white or yellowish precipitate becomes brown, owing to the formation of bismuthic acid:

$$\mathbf{BiO(OH)} + 2\,OH^- + Cl_2 \rightarrow H_2O + 2\,Cl^- + \mathbf{HBiO_3}.$$

2. **Ammonia** precipitates a white basic salt (not the hydroxide), the composition of which varies with the concentration and with the temperature.

3. **Alkali Carbonates** precipitate, according to the temperature and concentration, a number of basic carbonates; one of which is formed according to the following equation:

$$2\,Bi^{+++} + 3\,CO_3^{--} + H_2O \rightleftarrows 2\,\mathbf{Bi(OH)(CO_3)} + CO_2\uparrow.$$

4. **Sodium Phosphate** precipitates the white, granular phosphate, insoluble in dilute nitric acid, difficultly soluble in hydrochloric acid:

$$2\,HPO_4^{--} + Bi^{+++} \rightarrow H_2PO_4^- + \mathbf{BiPO_4}.$$

5. **Potassium Cyanide** precipitates the white hydroxide (not the cyanide). The cyanide is probably formed first, but it is hydrolyzed:

$$(a)\quad Bi^{+++} + 3\,CN^- \rightarrow \mathbf{Bi(CN)_3}.$$

$$(b)\quad \mathbf{Bi(CN)_3} + 3\,HOH = 3\,HCN + \mathbf{Bi(OH)_3}.$$

6. **Potassium Dichromate** added in excess precipitates yellow bismuthyl dichromate,

$$Cr_2O_7^{--} + 2\,Bi^{+++} + 2\,H_2O \rightleftarrows 4\,H^+ + \mathbf{(BiO)_2Cr_2O_7},$$

soluble in mineral acids, insoluble in caustic alkalies (difference from lead).

The precipitated dichromate is more soluble in acid and less soluble in alkalies than lead chromate.

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* In very concentrated KOH, $Bi(OH)_3$ dissolves on warming. On cooling, part of the $Bi(OH)_3$ is precipitated, and on dilution all of it. In this case the hydroxide acts as a weak acid, like antimony trioxide.

7. **Hydrogen Sulfide** precipitates brown bismuth sulfide,

$$2\,Bi^{+++} + 3\,H_2S \rightarrow \mathbf{Bi_2S_3} + 6\,H^+,$$

insoluble in cold dilute mineral acids and alkaline sulfides, soluble in hot dilute nitric acid, and in boiling, concentrated hydrochloric acid.

8. **Alkali Stannites** (an alkaline solution of stannous chloride) cause a black precipitation of metallic bismuth.* This very sensitive reaction is performed as follows: To a few drops of stannous chloride, add caustic alkali until the white precipitate at first produced dissolves clear. Add this sodium stannite solution to the cold bismuth solution; on shaking, a black precipitate immediately appears. The following reactions take place in this test:

$$Sn^{++} + 2\,OH^- \rightarrow \mathbf{Sn(OH)_2};$$

$$\mathbf{Sn(OH)_2} + 2\,OH^- \rightarrow 2\,H_2O + SnO_2^{--};$$

$$3\,SnO_2^{--} + 2\,Bi^{+++} + 6\,OH^- \rightarrow 3\,H_2O + 3\,SnO_3^{--} + \mathbf{2\,Bi}.$$

In making this test, a too concentrated caustic alkali solution should be avoided and the solution must be kept cold, otherwise the stannite itself may give a black precipitate of metallic tin (cf. pp. 179, 267):

$$2\,SnO_2^{--} + H_2O \rightarrow SnO_3^{--} + 2\,OH^- + \mathbf{Sn}.$$

If too little caustic potash is used, black stannous oxide will be thrown down in the cold, after long standing; quickly on boiling:

$$SnO_2^{--} + H_2O \rightarrow 2\,OH^- + \mathbf{SnO}.$$

9. **Potassium Iodide** precipitates black bismuth iodide,

$$Bi^{+++} + 3\,I^- \rightarrow \mathbf{BiI_3},$$

soluble in excess of the reagent, forming a yellow or orange solution:

$$\mathbf{BiI_3} + I^- \rightarrow [BiI_4]^-.$$

By diluting this last solution with not too much water, the black iodide is reprecipitated, which, on the addition of more water, is changed into orange-colored basic iodide:

$$\mathbf{BiI_3} + H_2O = 2\,HI + \mathbf{BiOI}.$$

10. **Metallic Zinc** precipitates metallic bismuth:

$$2\,Bi^{+++} + 3\,\mathbf{Zn} \rightarrow 3\,Zn^{++} + \mathbf{2\,Bi}.$$

11. **Sulfuric Acid** does not cause precipitation when added to acid solutions of bismuth salts. When the solution is evaporated until fumes of sulfuric acid are evolved, the resulting bismuth acid sulfate will dissolve in water giving a clear solution in most cases. After standing a long time, or sooner if considerable bismuth is present, a white

* Vanino and Treubert, *Ber.*, **1898**, 1113. The precipitate often contains BiO.

precipitate of bismuthyl pyrosulfate, $(BiO)_2S_2O_7 \cdot 3\,H_2O$, forms and this is sometimes mistaken for lead sulfate in the analytical procedure.

12. **Ammonium Thioacetate** causes the partial precipitation of bismuth sulfide in the cold and complete precipitation on boiling:

$$3\,CH_3COS^- + 2\,Bi^{+++} + 3\,H_2O \rightarrow 3\,HC_2H_3O_2 + \mathbf{Bi_2S_3} + 3\,H^+.$$

Sodium thiosulfate added to a bismuth salt containing not too much acid, gives at first a yellow coloration and finally a black precipitate of sulfide:

$$3\,H_2O + 2\,Bi^{+++} + 3\,S_2O_3^{--} \rightarrow \mathbf{Bi_2S_3} + 6\,H^+ + 3\,SO_4^{--}.$$

13. **Water** causes hydrolysis of all soluble bismuth salts and insoluble basic salts are precipitated. This is particularly true of the chloride:

$$Bi^{+++} + Cl^- + H_2O \rightarrow \mathbf{BiOCl} + 2\,H^+.$$

The precipitate dissolves readily in dilute, mineral acid but, unlike antimonyl chloride, SbOCl, it is not dissolved by tartaric acid. The precipitation of bismuthyl chloride is a characteristic reaction of bismuth and may take place, to some extent at least, when a chloride or even hydrochloric acid is added to a solution of bismuth nitrate.

Reactions in the Dry Way

Bismuth salts color the non-luminous flame a pale greenish white. Heated with soda on charcoal before the blowpipe, a brittle button of the metal is obtained, surrounded by a yellow incrustation of bismuth oxide.

On heating a compound of bismuth in the upper reducing flame (p. 68) of the Bunsen burner, the bismuth is reduced to metal, which is volatilized and burnt to oxide in the upper oxidizing flame. On holding a porcelain evaporating-dish (glazed on the outside and filled with water) just above the oxidizing flame, a barely visible deposit is obtained, which, on being treated with hydriodic acid, is changed to scarlet bismuth hydriodic acid:

$$Bi_2O_3 + 8\,HI = 3\,H_2O + 2\,H[BiI_4].$$

The hydriodic acid is most easily obtained by moistening a piece of asbestos, held in the loop of a platinum wire, in a solution of alcoholic iodine solution and then setting fire to the moist asbestos. By holding the burning asbestos under the dish, enough hydriodic acid is obtained to change the bismuth oxide into the red compound.

By breathing on this deposit, the color disappears, but reappears as soon as the moisture has evaporated. On exposure to fumes of ammonia (by blowing the vapors away from the stopper of an ammonia

bottle) the deposit is colored a beautiful orange, owing to the formation of the ammonium salt of the bismuth hydriodic acid,

$$H[BiI_4] + NH_3 \rightarrow NH_4[BiI_4],$$

which also becomes invisible on being breathed upon.

By moistening this coating with an alkaline solution of stannous chloride, black metallic bismuth is deposited.

COPPER, Cu. At. Wt. 63.57

Sp. Gr. = 9.84. M. Pt. = 1080° C.

Occurrence. — Copper occurs as native copper, Cu; cuprite, Cu_2O; chalcocite, Cu_2S; chalcopyrite, $CuFeS_2$; malachite, $Cu_2(OH)_2CO_3$; azurite, $Cu_3(OH)_2(CO_3)_2$ and atacamite, $Cu_2O(OH)Cl \cdot H_2O$.

Copper is a light red, ductile metal.

The proper solvent for copper is nitric acid:

$$3\,Cu + 8\,HNO_3 \rightarrow 3\,Cu^{++} + 6\,NO_3^- + 4\,H_2O + 2\,NO\uparrow.$$

Bright copper is not dissolved by hydrochloric acid alone, but in the presence of a weak oxidizing agent, e.g., ferric chloride, the solution of the metal is easily effected. Hot hydrobromic acid dissolves it with evolution of hydrogen, forming cuprous hydrobromic acid:

$$2\,Cu + 6\,HBr \rightleftarrows H_4[Cu_2Br_6] + H_2\uparrow.$$

At the beginning of this reaction the solution usually turns dark violet on account of the formation of the cupric salt of cuprous hydrobromic acid, owing to the copper being somewhat oxidized on the surface. In this case, however, the solution soon becomes colorless, owing to the reduction of the cupric salt by metallic copper. On adding water to the clear solution cuprous bromide is precipitated:

$$[Cu_2Br_6]^{=\!=} \rightarrow Cu_2Br_2 + 4\,Br^-.$$

Copper is not attacked by dilute sulfuric acid, but it dissolves in hot concentrated sulfuric acid, forming cupric sulfate with evolution of sulfur dioxide:

$$Cu + 2\,H_2SO_4 \rightarrow CuSO_4 + 2\,H_2O + SO_2\uparrow.$$

The behavior of copper toward acids can be understood by reference to the electromotive series (p. 41). As copper is below hydrogen in the series it can be oxidized by hydrogen ions only when the concentration of cupric ions is kept very low (cf. p. 43). Hydrobromic acid dissolves copper because a slightly ionized complex is formed. Sulfuric acid dissolves copper by virtue of the oxidizing power of the hexavalent sulfur.

Copper forms two oxides: red cuprous oxide, Cu_2O, and black cupric oxide, CuO.

Both oxides are basic anhydrides, forming cuprous and cupric salts. Salts of the cuprous series contain the bivalent cuprous group, Cu_2^{++}, while those of the cupric series contain the simple, bivalent copper atom Cu^{++}.

Copper is also known in the trivalent condition.* If a nitric acid solution of tellurous acid is evaporated to dryness with a little copper nitrate and the residue is treated with KOH solution (1 : 5) it dissolves. If to the clear solution 4 to 6 gms. of $(NH_4)_2(SO_4)_2$ are added, little by little, while the solution is at the temperature of the water bath, it becomes pink and the tellurium is present for the most part as telluric acid but to some extent as the potassium salt of telluro-cupric acid:

$$K[O \cdot Cu\begin{matrix}/O\backslash\\\backslash O/\end{matrix}TeO_3].$$

A. Cuprous Compounds

The cuprous compounds are extremely unstable, being oxidized quickly to cupric compounds. The best known cuprous salts are those with the halogens, the thiocyanate, the complex cyanides, the very unstable sulfate and the sulfite. Cuprous salts are colorless, insoluble in water, but readily soluble in concentrated halogen acids, forming colorless solutions. Such solutions contain the unstable cuprous halogen acids, probably of the formula $H_4[Cu_2X_6]$, in which "X" is either chlorine, bromine, or iodine. Salts are known which are derived from these acids, e.g., $K_4[Cu_2Cl_6]$.

The cuprous halogen acids are darkened by contact with air. The chloride becomes brownish black; the bromide, dark violet; probably due to the formation of cupric salts of the cuprous halogen acids.

The behavior of the cuprous halogen acids toward carbon monoxide is very important; the latter is readily absorbed, forming an unstable compound:

$$Cu_2Cl_2 + 2\,CO + 2\,H_2O \rightleftarrows Cu_2Cl_2 \cdot 2\,CO \cdot 2\,H_2O.$$

By boiling the solution the compound is decomposed into cuprous chloride and carbon monoxide; cuprous chloride is used in gas analysis for the absorption of this gas.

Reactions in the Wet Way

A solution of cuprous chloride in hydrochloric acid should be used, which may be prepared as follows: Dissolve 2 gms. of cupric oxide in 25 cc. of 6-normal hydrochloric acid, pour the solution into a flask and add 1.6 gm. of copper filings. Place several copper spirals in the

* Cf. MOSER, *Z. anorg. Chem.*, **54**, 119 (1907), and BRAUNER and KUZMA, *Ber.*, **1907**, 3382.

flask, one end reaching up to its neck, stopper the flask, invert it and let it stand several days. The originally dark solution will gradually become colorless and is then ready to be used for the following reactions:

1. **Potassium Hydroxide** produces in the cold a yellow precipitate of cuprous hydroxide,

$$Cu_2^{++} + 2\,OH^- \rightarrow \mathbf{Cu_2(OH)_2},$$

which loses water at the boiling temperature, changing to red cuprous oxide:

$$\mathbf{Cu_2(OH)_2} = H_2O + \mathbf{Cu_2O}.$$

2. **Hydrogen Sulfide** precipitates black cuprous sulfide,

$$Cu_2^{++} + H_2S \rightarrow 2\,H^+ + \mathbf{Cu_2S},$$

soluble in warm dilute nitric acid, forming blue cupric nitrate, with separation of sulfur:

$$3\,\mathbf{Cu_2S} + 16\,HNO_3 \rightarrow 8\,H_2O + 3\,S + 6\,Cu^{++} + 12\,NO_3^- + 4\,NO\uparrow.$$

3. **Potassium Cyanide** precipitates white cuprous cyanide,

$$Cu_2^{++} + 2\,(CN)^- \rightarrow \mathbf{Cu_2(CN)_2},$$

soluble in excess, forming colorless complex cuprocyanide anions:

$$\mathbf{Cu_2(CN)_2} + 6\,(CN)^- \rightarrow [Cu_2(CN)_8]^{----}.$$

This solution contains no appreciable quantity of cuprous ions, and gives no precipitation with potassium hydroxide or hydrogen sulfide. It is estimated that in a normal potassium cyanide solution the ratio of the concentration of the complex anion to that of simple cuprous ions is about $10^{26} : 1$. This fact is utilized in the separation of copper from cadmium.

In the absence of an excess of CN^- ions, however, an appreciable ionization takes place: $[Cu_2(CN)_8]^{----} \rightarrow Cu_2^{++} + 8\,CN^-$, and this ionization increases as the solution is diluted. From the diluted solutions the compounds $K_2[Cu_2(CN)_4]$, $K[Cu_2(CN)_3]$ and finally $Cu_2(CN)_2$ are obtained, which are of less complex nature.

All of these compounds, even in the solid state, are decomposed by hydrogen sulfide with precipitation of black cuprous sulfide. Consequently, *in order to prevent the precipitation of copper by hydrogen sulfide, considerable potassium cyanide must be added, more than enough to form the salt* $K_6[Cu_2(CN)_8]$.

B. Cupric Compounds

Cupric salts are either blue or green in aqueous solution; in the anhydrous state they are white or yellow.

The chloride, nitrate, sulfate and acetate are soluble in water; most of the remaining salts are insoluble in water, but readily soluble in acids.

Reactions in the Wet Way

A solution of copper sulfate should be used.

1. **Potassium Hydroxide** produces in the cold a blue precipitate of cupric hydroxide,

$$Cu^{++} + 2\,OH^- \rightarrow \mathbf{Cu(OH)_2},$$

which on boiling becomes changed into brownish-black cupric oxide.

$Cu(OH)_2$ is slightly amphoteric in nature and dissolves in very concentrated KOH or NaOH, particularly on warming, with a blue color. (Cf. p. 189.)

In the presence of tartaric acid, citric acid, and many other organic hydroxy-compounds, cupric hydroxide is not precipitated by the addition of caustic alkali, but the solution is colored an intense blue. If this alkaline solution is treated with *d*-glucose, aldehydes, arsenious acid or various other substances having a reducing power, yellow cuprous hydroxide is precipitated from the warm solution which is changed to red cuprous oxide on boiling. An alkaline solution of cupric salt containing tartaric acid is commonly used under the name of Fehling's solution. It may be prepared by mixing together equal volumes of a solution containing 34.64 gms. of crystallized copper sulfate in 500 cc. of water with a solution consisting of 173 gms. Rochelle salt and 52 gms. NaOH in 500 cc. of water. It is best to keep the solutions separate until they are to be used. Fehling's solution is a reagent for many kinds of sugar, aldehydes, hydroxylamine, etc.

2. **Ammonia.** — On adding ammonia cautiously to the solution of a cupric salt, a green, powdery precipitate of a basic salt is obtained, which is extremely soluble in an excess of the reagent, forming an azure-blue solution:

$$(a)\quad 2\,CuSO_4 + 2\,NH_4OH = (NH_4)_2SO_4 + \mathbf{Cu_2(OH)_2SO_4}.$$

$$(b)\quad \mathbf{Cu_2(OH)_2SO_4} + (NH_4)_2SO_4 + 6\,NH_3 = 2\,([Cu(NH_3)_4]SO_4 \cdot H_2O).$$

On adding alcohol to the concentrated blue solution, the above compound is precipitated as a blue-violet crystalline substance, which gradually loses ammonia on being heated, leaving behind the cupric salt. On conducting ammonia gas over an anhydrous copper salt, the ammonia is eagerly absorbed, with the formation of a complex cupric ammonia salt: $CuCl_2 + 6\,NH_3 = [Cu(NH_3)_6]Cl_2$.

These compounds (which contain as a maximum 6 NH_3 to one atom of copper) are perfectly analogous to the corresponding compounds of nickel, cobalt, and zinc. By the precipitation of the ammoniacal solution with alcohol, the compound with 4 NH_3 to one atom of copper is always obtained.

The ionization of the complex cation,

$$[Cu(NH_3)_4]^{++} \rightarrow Cu^{++} + 4\,NH_3\uparrow,$$

is slight in the presence of excess ammonia, but much more than that of the cuprocyanide ion (p. 229).

Ammonium salts tend to prevent the precipitation of the basic cupric salt because of the common ion effect upon the ionization of ammonium hydroxide, so that in adding ammonia to an acid solution of cupric salt often no precipitate is obtained. The blue color is perceptible even at considerable dilution and is often used as a basis of the quantity of copper present; the copper content is determined by the volume of standard potassium cyanide solution required to decolorize the solution. Nickelous solutions give a less intense blue color with ammonia and in case of doubt whether any copper is present in solution, the potassium ferrocyanide test is decisive.

Alkali hydroxide added to the blue, ammoniacal copper solution gives a dark blue of cupric hydroxide after some time. On boiling, all the copper can be precipitated as brownish black cupric oxide, CuO. A very dilute copper solution gives no noticeable blue color with ammonia; shaking with a few drops of phenol causes the blue color to appear on standing.

3. **Hydrogen Sulfide** precipitates from neutral or very slightly acid solutions, black cupric sulfide (possibly mixed with cuprous sulfide, Cu_2S), which has a tendency to form a colloidal solution (p. 58) and run through the filter:

$$Cu^{++} + H_2S \rightarrow 2\,H^+ + \mathbf{CuS}.$$

To prevent the formation of a colloidal solution, the solution must contain some electrolyte; the hydrochloric acid present when the precipitation is made is usually sufficient. Another difficulty frequently encountered is due to the readiness with which a part of the cupric sulfide precipitate is oxidized to sulfate by contact with the air. Thus if a filter containing copper sulfide is allowed to stand in the air, a little cupric sulfate is formed which is soluble in water. Many cases where the cupric sulfide apparently runs through the filter are explained in this way. In filtering a copper sulfide precipitate the rule should be never to let the filter drain completely until the filtration and washing is over, and the washing should be with dilute hydrogen sulfide water, which serves to prevent any oxidation.

Copper sulfide is soluble in hot dilute nitric acid, but insoluble in boiling dilute sulfuric acid (difference from cadmium); it is soluble in potassium cyanide, forming potassium cuprous cyanide. From a solution of the latter salt the copper cannot be precipitated by hydrogen sulfide.

Copper sulfide is appreciably soluble in ammonium sulfide, but is insoluble in potassium or sodium sulfide * (difference from mercury).

* In solutions of alkali polysulfides, particularly out of contact with the air, cupric sulfide dissolves appreciably with the formation of compounds of the type $NH_4[CuS_4]$ and $K[CuS_4]$. Cf. Hofmann and Höchtlen, *Ber.*, **36**, 3900 (1903), and Biltz and Herms, *ibid.*, **40**, 974 (1907).

4. **Potassium Cyanide** produces, at first, yellow cupric cyanide, which immediately loses dicyanogen, forming white cuprous cyanide. The latter, as we have already seen, forms soluble potassium cuprous cyanide with more potassium cyanide:

$$2\,Cu^{++} + 4\,CN^- \rightarrow 2\,\mathbf{Cu(CN)_2};$$

$$2\,\mathbf{Cu(CN)_2} \rightarrow (CN)_2\uparrow + \mathbf{Cu_2(CN)_2};$$

$$\mathbf{Cu_2(CN)_2} + 6\,(CN)^- \rightarrow [Cu_2(CN)_6]^{----}.$$

On adding sufficient potassium cyanide to the blue ammoniacal cupric solution, the complex compound will be decolorized, forming potassium cuprocyanide, and the reduction of the cupric salt to cuprous condition in ammoniacal solution is accomplished at the expense of cyanide ions which are oxidized to cyanate:

$$2\,[Cu(NH_3)_4]^{++} + 9\,(CN)^- + 2\,OH^- \rightleftarrows [Cu_2(CN_8)]^{----} + (CNO)^- + 8\,NH_3 + H_2O.$$

The ratio of simple Cu^+ ions to complex $[Cu_2(CN)_8]^{----}$ ions has been estimated to be as $1 : 10^{26}$ in a normal solution of potassium cyanide.

Hydrogen sulfide will not precipitate cupric sulfide from the colorless solution of potassium cuprocyanide provided sufficient potassium cyanide is present (difference from cadmium). Sometimes, when considerable copper salt is present, the introduction of H_2S causes the formation of a red crystalline precipitate of hydrorubianic acid, $(CSNH_2)_2$. Cf. p. 336.

5. **Potassium Thiocyanate,** KCNS, precipitates black cupric thiocyanate,

$$Cu^{++} + 2\,(CNS)^- \rightarrow \mathbf{Cu(CNS)_2},$$

which is gradually changed into white cuprous thiocyanate, or immediately on adding sulfurous acid:

$$2\,\mathbf{Cu(CNS)_2} + SO_3^{--} + H_2O \rightarrow 2\,CNS^- + SO_4^{--} + 2\,H^+ + \mathbf{Cu_2(CNS)_2}.$$

Cuprous thiocyanate is insoluble in water, dilute hydrochloric acid, and sulfuric acid.

6. **Alkali Xanthates** produce in solutions of cupric salts, at first, a brownish-black precipitate of cupric xanthate, which splits off dixanthogen, forming finally yellow cuprous xanthate:

$$2\,\mathbf{NaS \cdot \overset{\overset{S}{\|}}{C}OC_2H_5} + Cu^{++} \rightarrow 2\,Na^+ + \mathbf{Cu(S \cdot \overset{\overset{S}{\|}}{C}OC_2H_5)_2}.$$

Sodium xanthate

$$2\,\mathbf{Cu(S \cdot \overset{\overset{S}{\|}}{C} \cdot OC_2H_5)_2} \rightarrow \underset{\text{Cuprous xanthate}}{\mathbf{Cu_2(S\overset{\overset{S}{\|}}{C}OC_2H_5)_2}} + \underset{\text{Dixanthogen}}{\mathbf{(S\overset{\overset{S}{\|}}{C}OC_2H_5)_2}}.$$

The reagent, sodium xanthate, is readily obtained by mixing carbon disulfide with sodium alcoholate:

$$CS_2 + NaOC_2H_5 \rightarrow NaS \cdot \overset{\overset{S}{\|}}{C} \cdot OC_2H_5.$$

The alkali xanthates are not used as reagents in testing for copper, but cupric salts are used in testing for xanthates. The reaction is used for the detection of carbon disulfide in gas mixtures; the gases are allowed to act upon sodium alcoholate, whereby sodium xanthate is formed if carbon disulfide is present, and the solution after neutralizing with acetic acid is tested for xanthate by means of a solution of cupric salt.

7. **Potassium Ferrocyanide,** $K_4[Fe(CN)_6]$, produces in neutral and acid solutions an amorphous precipitate of reddish-brown cupric ferrocyanide,

$$2\,Cu^{++} + [Fe(CN)_6]^{=\,=} \rightarrow \mathbf{Cu_2[Fe(CN)_6]},$$

insoluble in dilute acids, but soluble in ammonia with a blue color (difference from molybdenum ferrocyanide which dissolves in ammonia, forming a yellow solution). It is also decomposed by potassium hydroxide: in the cold, light-blue cupric oxide and potassium ferrocyanide are formed, while, on warming, black cupric oxide is obtained (difference from uranium, which yields the yellow uranate both with ammonia and sodium or potassium hydroxide).

8. **Ammonium Thioacetate** completely precipitates copper sulfide from hot solutions, even in the presence of acid:

$$C_2H_3OS^- + Cu^{++} + H_2O \rightarrow \mathbf{CuS} + HC_2H_3O_2 + H^+.$$

Sodium Thiosulfate decolorizes a neutral or acid solution of a copper salt and, on boiling the acid solution, a reddish brown precipitate is formed which eventually becomes black cuprous sulfide:

$$2\,Cu^{++} + 2\,S_2O_3^{-\,-} + 2\,H_2O \rightarrow \mathbf{Cu_2S} + 4\,H^+ + 2\,SO_4^{-\,-} + \mathbf{S}.$$

9. **Acetylene** gas introduced into an ammoniacal alkali tartrate solution, in which the copper has been reduced to the cuprous condition by hydroxylamine, gives a reddish-brown, flocculent precipitate of cuprous acetylide, $C_2Cu_2 \cdot H_2O$. By this means copper ions can be separated from many other cations.

10. **Potassium Iodide** precipitates pale-pink cuprous iodide but, owing to the color of the liberated iodine, the precipitate appears green to reddish yellow.

$$2\,Cu^{++} + 4\,I^- \rightarrow \mathbf{Cu_2I_2} + I_2.$$

In the presence of a reducing agent, no free iodine is obtained. In quantitative analysis the copper content is determined by measuring

the volume of sodium thiosulfate solution required to react with the iodine:

$$I_2 + 2\,S_2O_3^{--} \rightarrow S_4O_6^{--} + 2\,I^-.$$

Potassium iodide added to a dilute solution of a cupric salt gives a yellow coloration due to the liberated iodine.

11. **Potassium Bromide** solution mixed with concentrated sulfuric acid and, when cold, covered with a little copper salt solution gives a beautiful bluish red color at the zone of contact of the two solutions. On shaking, the whole solution becomes red. According to Sabatier, the coloration is caused by the formation of $CuBr_2 \cdot HBr \cdot 2\,H_2O$.

When considerable copper is present, a black precipitate of copper bromide is obtained. Dilution with water causes the color to disappear. Stannous ions prevent the reaction by reduction of the cupric ions. If sulfur dioxide is added to the dark bluish red solution, a white precipitate of cuprous bromide is obtained.

12. **Cupferron** added to an acid solution of a cupric salt, precipitates the copper salt of phenyl-nitroso-hydroxylamine.

$$2\,[C_6H_5(NO)NO]^- + Cu^{++} \rightarrow \mathbf{Cu[C_6H_5(NO)NO]_2},$$

which dissolves in ammonia giving a blue solution.

13. **Iron** added to a solution of a copper salt precipitates red, metallic copper:

$$Cu^{++} + \mathbf{Fe} \rightarrow Fe^{++} + \mathbf{Cu}.$$

Other metals, such as zinc, aluminium, etc., which are above copper in the voltage series will give a similar reaction.

The copper may be deposited upon platinum, and thus examined more easily, by using a strip of platinum foil in contact with zinc, tin, aluminium, etc. In this case an electric couple is formed and the platinum acts as cathode while the other metal, as anode, dissolves.

14. **Alkali Carbonates** give a greenish-blue precipitate of basic carbonate; on standing with an excess of the reagent the precipitation is nearly complete and a crystalline salt, $3\,CuCO_3 \cdot 3\,Cu(OH)_2 \cdot H_2O$, is formed. This precipitate dissolves in ammonia with a blue color and in potassium cyanide solution to form a colorless solution.

Ammonium salts and certain organic substances form complex anions with copper and prevent this reaction.

Reactions in the Dry Way

The borax, or salt of phosphorus, bead is green in the oxidizing flame when strongly saturated with the copper salt; blue if containing only a small amount. The reducing flame decolorizes the bead unless too much copper is present; in such a case it is reddish brown and

opaque, owing to the separation of copper. Traces of copper may be determined with certainty as follows: To the slightly bluish bead produced by the oxidizing flame, add a trace of tin or of a tin compound. Heat the bead in the oxidizing flame until the tin has completely dissolved, then bring it slowly into the reducing flame and finally quickly remove it. The bead now appears colorless when hot, but ruby-red and transparent when cold. If, however, the bead is kept too long in the reducing flame, it remains colorless; but the ruby-red color may be produced by cautious oxidation. This reaction is very sensitive, and can also be used for the detection of tin.

Heated with charcoal before the blowpipe (or better still with the charcoal stick), spongy metal is obtained.

Copper salts color the flame blue or green. Moistening with hydrochloric acid increases the sensitiveness of this test.

CADMIUM, Cd. At. Wt. 112.40

Sp. Gr. = 8.6. M. Pt. = 321°. B. Pt. = 770° C.

Occurrence. — Cadmium is usually associated with zinc in its ores. It is also found as greenockite, CdS, hexagonal; and as the oxide, CdO,* isometric.

The most important commercial salt is the sulfate, $3\,CdSO_4 \cdot 8\,H_2O$. It is not easily recrystallized. To purify the salt, the concentrated aqueous solution is treated with alcohol, and the crystals that are deposited thereby are filtered, washed with alcohol and dried upon blotting paper.

Cadmium is a silver-white, ductile metal. Heated in the air, it changes to brown cadmium oxide. The proper solvent for cadmium is nitric acid. Dilute hydrochloric and sulfuric acids dissolve it but slowly, with evolution of hydrogen. Cadmium forms two oxides: black cadmium suboxide, Cd_2O, and light or dark-brown cadmium oxide, CdO.

Cadmium suboxide (whose existence is doubted) is formed with cadmium oxide in small amounts when the metal is burned in the air. It is also said to be formed, like lead suboxide, by gently heating the oxalate away from air. There are no cadmium salts derived from this oxide. Cadmium forms only one series of salts, in which cadmium is bivalent.

Cadmium salts are mostly colorless, though the sulfide is yellow or orange. Most of the salts are insoluble in water, but readily soluble

* With smithsonite in the zinc deposits of Monte Poni, Sardinia. *Chem. Ztg.*, **1901**, 561.

in mineral acids. The chloride, nitrate and sulfate are soluble in water.

Reactions in the Wet Way

1. **Potassium Hydroxide** precipitates white, amorphous cadmium hydroxide, insoluble in an excess of the reagent (difference from zinc and lead):

$$Cd^{++} + 2\,OH^- \rightarrow \mathbf{Cd(OH)_2}.$$

On gently igniting the hydroxide the brown oxide is obtained, which becomes darker on stronger ignition. The ignition of cadmium nitrate yields the black crystalline oxide.

2. **Ammonia** also precipitates the white hydroxide, soluble in excess (difference from lead), forming complex cadmium ammonia compounds, as with zinc, nickel, etc.

$$\mathbf{Cd(OH)_2} + 4\,NH_3 \rightarrow [Cd(NH_3)_4]^{++} + 2\,(OH)^-.$$

In the presence of normal ammonium hydroxide the ratio of the concentration of the complex anion to that of the simple cadmium cation is about $10^7 : 1$. In pure water, the ionization takes place to a much greater extent; by diluting with water and boiling, cadmium hydroxide is reprecipitated from the solution of the cadmium ammonium compound.

3. **Alkali** and **Ammonium Carbonates** precipitate the white basic carbonate insoluble in excess.

Ammonium salts tend to prevent the precipitation but, on boiling, ammonia gas is evolved and the precipitation is complete. The precipitate dissolves in potassium cyanide solution.

4. **Potassium Cyanide** precipitates white, amorphous cadmium cyanide, readily soluble in excess:

$$Cd^{++} + 2\,(CN)^- \rightarrow \mathbf{Cd(CN)_2},$$

$$\mathbf{Cd(CN)_2} + 2\,(CN)^- \rightarrow [Cd(CN)_4]^{--}.$$

From the solution of cadmium potassium cyanide the above-mentioned reagents produce no precipitation. In a normal solution of potassium cyanide the concentration of the complex anion to that of the simple cadmium cation is $10^{17} : 1$. This is evidently a much weaker complex than the cuprocyanide anion and for this reason cadmium sulfide, though its solubility product is much larger than that of cupric sulfide, is precipitated by hydrogen sulfide (difference from copper):

$$[Cd(CN)_4]^{--} + H_2S \rightarrow 2\,CN^- + 2\,HCN + \mathbf{CdS}.$$

5. **Hydrogen Sulfide** produces precipitates varying in color from a canary-yellow, orange to almost brown, according to the conditions.

In neutral solution, whether hot or cold, light-yellow cadmium sulfide is obtained in a condition hard to filter. From acid solutions (containing in 100 cc. from 2 to 10 cc. of conc. H_2SO_4, or from 2 to 5 cc. of conc. HCl) yellow precipitates which turn orange in color are at once thrown down and are easy to filter. The latter precipitates are not pure CdS, but always contain more or less Cd_2Cl_2S or $Cd_2(SO_4)S$. For this reason cadmium should not be determined quantitatively as the sulfide.

Cadmium sulfide is insoluble in alkaline sulfides (difference from arsenic), but is soluble in considerable hydrochloric acid, warm dilute nitric acid, and hot dilute sulfuric acid (difference from copper). It is also insoluble in potassium cyanide solution (difference from copper).

6. **Ammonium Sulfide** produces a yellow precipitate of cadmium sulfide, which has a tendency to form colloidal solutions and pass through the filter. The presence of a concentrated salt solution prevents this (cf. p. 231).

7. **Potassium Ferrocyanide** gives a white precipitate. (Cf. zinc.)

8. **Ammonium Perchlorate** gives a crystalline precipitate of cadmium perchlorate, $Cd(ClO_4)_2$. (Difference from copper.)

9. **Potassium Thiocyanate** has no effect upon cadmium solutions. (Difference from copper.)

10. **Metals,** like iron, tin, zinc, etc., do not precipitate cadmium from acid solutions. (Difference from copper.)

Reactions in the Dry Way

Cadmium compounds, heated on charcoal with soda, give a brown incrustation of cadmium oxide.

If a compound of cadmium oxide is reduced in the upper reducing flame of the Bunsen burner, the cadmium oxide is changed to metal, which volatilizes, and, in the upper oxidizing flame, goes back to oxide, which will be deposited as a brown coating if a glazed porcelain dish filled with water is held just above the flame. This oxide always contains some suboxide mixed with it, and has the property of reducing silver oxide to metal; so that if the coating of oxide is moistened with silver nitrate solution a black deposit of metallic silver will be obtained:

$$Cd_2O + 2\,Ag^+ \rightarrow Cd^{++} + CdO + 2\,Ag.$$

This reaction is very sensitive.

If it is desired to test the precipitate produced by hydrogen sulfide for cadmium in this way, first roast the sample in the oxidizing flame and then treat it as just described.

ARSENIC, As. At. Wt. 74.96

Sp. Gr. = 5.73

Occurrence. — Arsenic is widely distributed in nature, being found in small amounts in almost all sulfides, as, for example, sphalerite and pyrites: therefore almost all the zinc and sulfuric acid of commerce contain arsenic.

Arsenic occurs native in kidney-shaped masses; also in the form of its dimorphous oxide, As_2O_3, as isometric arsenolite and orthorhombic claudetite.

Mimetite, $Pb_5(AsO_4)_3Cl$, hexagonal, isomorphous with apatite, pyromorphite, and vanadinite, is a well-known mineral containing arsenic oxide.

The most important sources of arsenic are the sulfides, arsenides, and sulfo salts: realgar, As_2S_2, monoclinic; orpiment, As_2S_3, monoclinic; arsenopyrite, FeAsS, orthorhombic; niccolite, NiAs, hexagonal; löllingite, $FeAs_2$, orthorhombic; smaltite, $(Co,Ni,Fe,)As_2$, isometric; and proustite, $As(SAg)_3$, rhombohedral.

Metallic arsenic is a steel-gray, brittle substance. On being heated it sublimes, giving off a characteristic garlic odor. The merest trace of arsenic may be recognized by this odor, which is said to be due to the formation of a yellow, allotropic form of arsenic. *The vapors are poisonous.* The stable molecule of arsenic contains, like phosphorus, four atoms, (As_4).

Arsenic is insoluble in hydrochloric acid, but readily soluble in nitric acid and in aqua regia.

Dilute nitric acid dissolves arsenic, forming arsenious acid:

$$As_4 + 4\,HNO_3 + 4\,H_2O = 4\,H_3AsO_3 + 4\,NO\uparrow.$$

Concentrated nitric acid and aqua regia dissolve it, forming arsenic acid:

$$3\,As_4 + 20\,HNO_3 + 8\,H_2O = 12\,H_3AsO_4 + 20\,NO\uparrow.$$

Sodium hypochlorite solution also dissolves arsenic:

$$10\,NaClO + As_4 + 6\,H_2O = 4\,H_3AsO_4 + 10\,NaCl.$$

Arsenic belongs to the same natural group of elements as nitrogen and phosphorus, and forms two oxides, As_2O_3 and As_2O_5.

In reality the symbol of the lower oxide is As_4O_6, but it is customary to use the simpler symbol, As_2O_3.

A. Arsenious Compounds

Arsenic trioxide is formed by the combustion of arsenic in the air as white, glistening crystals of regular octahedrons. If the vapors of

the trioxide are allowed to cool slowly, they solidify to an amorphous glass (arsenic glass), which gradually becomes crystalline (white and opaque, like porcelain).

Arsenic trioxide is known in three different modifications: isometric arsenic trioxide (white arsenic); monoclinic arsenic trioxide, and amorphous, glassy arsenic trioxide.

The monoclinic modification is difficultly soluble in water (80 cc. of cold water dissolve 1 gm. As_2O_3); while the amorphous, glassy modification is much more soluble (25 cc. of cold water dissolve 1 gm. arsenic trioxide). By treatment of the ordinary modification (white arsenic) with water, it is not readily wet by the latter; it floats like flour, and this behavior is very characteristic.

The trioxide dissolves quite readily in hydrochloric acid, particularly on warming, from which solution it often separates out, on cooling, in a beautiful, crystalline, anhydrous condition.

Acting as an acid anhydride it dissolves readily in alkalies, forming easily soluble arsenites:

$$As_2O_3 + 6\,OH^- \rightarrow 3\,H_2O + 2\,AsO_3^{---};$$
$$As_2O_3 + 3\,CO_3^{--} \rightarrow 3\,CO_2\uparrow + 2\,AsO_3^{---}.$$

The tri-metal arsenites derived from the ortho acid H_3AsO_3 are usually unstable. Silver arsenite, Ag_3AsO_3, is the only well-known salt of this type. The alkali arsenites are derived from metarsenious acid, $HAsO_2$, from pyroarsenious acid, $H_4As_2O_5$ or from a polyarsenious acid such as $H_6As_4O_9$. The only sodium and potassium salts known are of the types $KAsO_2$ and $K_2H_4As_2O_9$; of ammonium, $(NH_4)_4As_2O_5$. In alkaline solution, however, we may assume that AsO_3^{---} ions are present.

Free arsenious acid, H_3AsO_3, has never been isolated; as a very weak acid it breaks down, like carbonic acid, into water and the anhydride.

Arsenic combines with chlorine directly, like phosphorus, forming the chloride, $AsCl_3$, which behaves exactly like the chloride of arsenious acid, similar to PCl_3. It is a colorless liquid, boiling at 134° C., and is decomposed quantitatively, like all acid chlorides, with water:

$$AsCl_3 + 3\,H_2O \rightleftarrows 3\,HCl + H_3AsO_3.$$

The aqueous solution of arsenic trichloride and the solution of the trioxide in dilute hydrochloric acid, contain the arsenic as arsenious acid. As the concentration of the hydrochloric acid increases, the amount of arsenic trichloride increases, until in very concentrated hydrochloric acid the arsenic is present almost entirely as trichloride. By boiling a solution of arsenic trichloride in hydrochloric acid, arsenic trichloride is driven off as a gas. If hydrochloric acid is conducted into the solution at the same time (so that the concen-

tration of the hydrochloric acid is kept as large as possible), all the arsenic can be volatilized from the solution as arsenious chloride. On evaporating a hydrochloric acid solution of arsenious acid, arsenious chloride constantly escapes, so that all the arsenic may be volatilized. If, however, the arsenic is present in the form of arsenic acid, no arsenic is lost during the evaporation of the solution.

Reactions of Arsenious Acid in the Wet Way

The arsenites of the alkalies are soluble in water; the remaining arsenites are insoluble in water, but soluble in acids.

1. **Hydrogen Sulfide** precipitates from acid solutions yellow, flocculent arsenic trisulfide:

$$2\,As(OH)_3 + 3\,H_2S = 6\,H_2O + \mathbf{As_2S_3},$$

$$2\,AsCl_3 + 3\,H_2S = 6\,HCl + \mathbf{As_2S_3}.$$

Arsenious sulfide is insoluble in acids; even boiling 6-normal hydrochloric acid does not dissolve it, but by long boiling with 12-normal hydrochloric acid it is slowly changed to volatile $AsCl_3$ and H_2S. Concentrated nitric acid oxidizes it to arsenic acid and sulfuric acid:

$$3\,\mathbf{As_2S_3} + 28\,HNO_3 + 4\,H_2O = 9\,H_2SO_4 + 28\,NO\uparrow + 6\,H_3AsO_4.$$

The sulfide dissolves more readily in ammoniacal hydrogen peroxide:

$$\mathbf{As_2S_3} + 14\,H_2O_2 + 12\,OH^- \rightarrow 20\,H_2O + 3\,SO_4^{--} + 2\,AsO_4^{---}.$$

It is also dissolved by alkalies, ammonium carbonate, and alkali sulfides:

$$\mathbf{As_2S_3} + 6\,OH^- \rightarrow 3\,H_2O + AsO_3^{---} + AsS_3^{---};$$

$$\mathbf{As_2S_3} + 3\,CO_3^{--} \rightarrow 3\,CO_2\uparrow + AsO^{---} + AsS_3^{---};$$

$$\mathbf{As_2S_3} + 3\,S^{--} \rightarrow 2\,AsS_3^{---}.$$

Just as the anhydride, As_2O_3, can be referred to the acid, H_3AsO_3, so the thioanhydride, As_2S_3, can be referred to the thioarsenious acid, H_3AsS_3, which is not capable of existence in the free state, but is known in the form of its salts. If one of the latter salts is acidified, then thioarsenious acid is set free; but it immediately loses H_2S, forming the insoluble thioanhydride:

$$2\,AsS_3^{---} + 6\,H^+ \rightarrow 3\,H_2S + \mathbf{As_2S_3}.$$

On treating a mixture of thioarsenite and arsenite with acid, arsenic trisulfide is also precipitated:

$$AsO_3^{---} + AsS_3^{---} + 6\,H^+ \rightarrow 3\,H_2O + \mathbf{As_2S_3}.$$

In this last case precipitation is quantitative only when the solution is dilute; from a concentrated solution H_2S escapes, so that more H_2S must be conducted into the solution in order to precipitate all the arsenic.

Boiling a solution of arsenite and thioarsenite with bismuth hydroxide, carbonate or nitrate, etc., results in the formation of black bismuth sulfide:

$$AsS_3^{---} + 2\,Bi(OH)_3 \rightarrow Bi_2S_3 + AsO_3^{---} + 3\,H_2O.$$

With cupric oxide, or a soluble copper salt, black cuprous sulfide is formed and the arsenic is oxidized to arsenate:

$$5\,CuO + AsS_3^{---} + AsO_3^{---} \rightarrow 2\,Cu_2S + 2\,AsO_4^{---} + CuS.$$

This property of forming thio-salts accounts for the fact that hydrogen sulfide produces no precipitation from normal arsenites, and only a partial precipitation of As_2S_3, from mono- and dimetallic salts:

$$AsO_3^{---} + 3\,H_2S \rightarrow 3\,H_2O + AsS_3^{---}.$$

$$6\,HAsO_3^{--} + 15\,H_2S \rightarrow 18\,H_2O + As_2S_3 + 4\,AsS_3^{---}.$$

$$3\,H_2AsO_3^{-} + 6\,H_2S \rightarrow 9\,H_2O + As_2S_3 + AsS_3^{---}.$$

Consequently, in order to precipitate arsenic completely as trisulfide, it is always necessary that the solution should contain enough free acid to prevent the formation of soluble sulfo-salts.

Igniting arsenic trisulfide with sodium carbonate and nitrate cause the formation of sulfate and arsenate:

$$5\,As_2S_3 + 16\,Na_2CO_3 + 28\,NaNO_3 \rightarrow 10\,Na_3AsO_4 + 15\,Na_2SO_4 + 16\,CO_2\uparrow + 14\,N_2\uparrow.$$

Heating in a stream of chlorine results in the volatilization of arsenic trichloride. The same reaction takes place when the sulfide is heated in a tube in a current of air with a mixture of five parts ammonium chloride and one of ammonium nitrate.

2. **Silver Nitrate** produces in neutral solutions of arsenites a *yellow* precipitate of silver orthoarsenite (difference from arsenic acid),

$$AsO_3^{---} + 3\,Ag^+ \rightarrow Ag_3AsO_3,$$

soluble in nitric acid and ammonia:

$$Ag_3AsO_3 + 3\,H^+ \rightarrow 3\,Ag^+ + H_3AsO_3.$$

$$Ag_3AsO_3 + 6\,NH_3 \rightarrow 3\,Ag(NH_3)_2^+ + AsO_3^{---}.$$

The first reaction is caused by the formation of nonionized arsenious acid, which, in the presence of an excess of H^+ ions furnishes even less AsO_3^{---} ions than are formed by the very slightly soluble Ag_3AsO_3 in contact with water. The solubility in ammonia is due to the fact that the $[Ag(NH_3)_2]^+$ ion in the presence of an excess of NH_3 furnishes fewer simple Ag^+ cations than Ag_3AsO_3 in contact with water.

In aqueous solutions of the mono- and dimetallic salts the precipitation is incomplete:

$$3\,As{-}OH + 3\,AgNO_3 = 3\,KNO_3 + 2\,H_3AsO_3 + Ag_3AsO_3.$$
$$\quad\;\; OK$$

$$H_2AsO_3^{-} + 3\,Ag^+ \rightleftarrows Ag_3AsO_3 + 2\,H^+.$$

In order to make the precipitation quantitative, an alkali (preferably ammonia) must be added. As, however, the solution already reacts alkaline, it is difficult to reach the exact neutral point. Usually too much ammonia is added. As a rule in qualitative analysis it is unnecessary to accomplish complete precipitation in this test, as the *color* of the silver precipitate suffices to show whether an *arsenite* or an *arsenate* is present. To make the precipitation practically complete, add ammonia drop by drop to a solution of silver nitrate until the precipitate of silver oxide that first forms redissolves; the solution then contains complex $[Ag(NH_3)_2]^+$ cations instead of simple Ag^+ ions. Add this reagent to the arsenite solution which has been made weakly acid with nitric acid:

$$H_3AsO_3 + 3\,[Ag(NH_3)_2]^+ + 3\,H^+ \rightarrow 6\,NH_4^+ + \mathbf{Ag_3AsO_3}.$$

The addition of the nitric acid is necessary, as otherwise the solution will become ammoniacal, dissolving a part of the silver arsenite.

In case the solution to be tested contains also a chloride, it should be acidified with nitric acid and the chloride precipitated as silver chloride by an excess of silver nitrate, and filtered off. To the filtrate, dilute ammonia should be added cautiously. At the neutral zone formed by the ammonia above the acid solution, a yellow precipitate of silver arsenite will appear. This reaction is very sensitive.

3. **Magnesium Ammonium Chloride** produces no precipitation in dilute arsenite solutions in the presence of ammonia (difference from arsenic acid).

4. **Iodine Solution** is decolorized by arsenious acid, the latter being oxidized to arsenic acid:

$$H_2AsO_3^- + I_2 + H_2O \rightleftarrows 2H^+ + 2I^- + H_2AsO_4^-.$$

To make the reaction take place quantitatively in the direction left to right it is necessary to keep the solution neutral; to make the reaction take place quantitatively in the direction right to left it is necessary to add a considerable excess of hydrogen ions. This is in strict accord with the mass-action principle. This behavior has been explained by assuming that free hydriodic acid is a better reducing agent than iodide ions, but it is more probable that the effect of the acid upon the stability of the arsenic compounds is more important. In alkaline solutions, the arsenic is more stable in the higher state of oxidation and, for this reason, the arsenite solutions have strong reducing powers in neutral or alkaline solutions. Arsenious acid is amphoteric and forms, as we have seen, a trichloride and trisulfide. In the presence of an excess of hydrogen ions from some other source, arsenious acid will not ionize appreciably as an acid and the tendency will be to form As^{+++} cations. Probably arsenic acid is also amphoteric, though to a much less extent. In strongly acid solutions, the ionization of the arsenic acid is repressed to some extent and there is a tendency to form As^{+++++} cations, but these are far less stable than As^{+++} cations and, therefore, in strongly acid solutions an arsenate acts as a vigorous oxidizing agent.

The explanation is in the line with the results obtained in the study of reduction potentials (cf. p. 44). The addition of acid decidedly increases the oxidizing power of arsenic acid, but slightly diminishes the reduction power of an iodide.

To keep the solution neutral when it is desired to oxidize an arsenite by means of iodide, it is not advisable to use caustic alkali solution, as this itself reacts with iodine, forming iodide and hypo-iodite. Sodium bicarbonate is generally used:

$$HCO_3^- + H^+ \rightarrow H_2O + CO_2\uparrow.$$

Equally satisfactory is sodium phosphate, which forms with hydrogen ions the very slightly ionized $H_2PO_4^-$ ions. A normal alkali carbonate can be used if the solution is saturated with carbonic acid; there are then not enough OH^- ions formed by the hydrolysis of the normal carbonate to react with the iodine.

5. **Stannous Chloride (Bettendorff's Test).** — On adding to concentrated hydrochloric acid a few drops of an arsenite solution and then $\frac{1}{2}$ cc. of a saturated solution of stannous chloride in hydrochloric acid, the solution quickly becomes brown and then black, owing to the deposition of metallic arsenic. The reaction takes place more readily on warming, but a dilute aqueous solution will not give the reaction. In concentrated hydrochloric acid, however, the arsenic is all present as trichloride, and this is reduced by the stannous chloride, while arsenious acid is not:

$$2\,As^{+++} + 3\,Sn^{++} \rightarrow 3\,Sn^{++++} + 2\,As.$$

6. **Ammonium Thioacetate** added to a hot, acid solution of an arsenite produces complete precipitation of arsenic trisulfide:

$$3\,C_2H_3OS^- + 2\,AsO_3^{---} + 9\,H^+ \rightarrow 3\,HC_2H_3O_2 + \mathbf{As_2S_3} + 3\,H_2O.$$

Sodium Thiosulfate also causes complete precipitation of the arsenic:

$$3\,S_2O_3^{--} + 2\,AsO_3^{---} + 6\,H^+ \rightarrow \mathbf{As_2S_3} + 3\,SO_4^{--} + 3\,H_2O.$$

7. **Cupric Sulfate** does not precipitate the arsenic from an aqueous solution of arsenious acid; the addition of a little alkali hydroxide causes the formation of yellowish green cupric arsenite, which is soluble in an excess of caustic alkali forming a blue solution, but on boiling red cuprous oxide is precipitated. This is a sensitive reaction for distinguishing arsenious from quinquevalent arsenic compounds although it must be remembered that many organic reducing agents precipitate cuprous oxide under similar conditions.

8. **Potassium Iodide** added to a hot, acid solution forms red arsenious iodide:

$$AsO_3^{---} + 6\,H^+ + 3\,I^- \rightarrow \mathbf{AsI_3} + 3\,H_2O.$$

In concentrated solution, a red precipitate is obtained.

Often, in quantitative analysis, an arsenate is reduced to arsenite by treating the acid solution with a moderate excess of potassium iodide:

$$AsO_4^{---} + 2\,I^- + 2\,H^+ \rightarrow AsO_3^{---} + H_2O + I_2.$$

This causes the liberation of red iodine and, if this is boiled off, the color of arsenic trioxide appears when the solution is concentrated. In fact it is difficult to tell when the iodine is all gone and practically impossible to distill off the last traces of iodine without losing some arsenic iodide.

B. Compounds of Arsenic Pentoxide

Arsenic pentoxide, which may be obtained by heating arsenic acid, is a white, fusible substance, and is changed by strong ignition into arsenic trioxide: $As_2O_5 = As_2O_3 + O_2\uparrow$. Arsenic pentoxide is quite soluble in water, forming arsenic acid:

$$As_2O_5 + 3\,H_2O = 2\,H_3AsO_4.$$

Arsenic acid itself may be obtained in the solid state in the form of orthorhombic prisms corresponding to the formula $2\,H_3AsO_4 \cdot H_2O$. At 100° C. water escapes, orthoarsenic acid, H_3AsO_4, being left behind as a crystalline powder.

By gentle ignition more water is given off, forming pyroarsenic acid, $H_4As_2O_7$, which on further ignition is changed to metarsenic acid, $HAsO_3$. In this respect arsenic acid acts exactly like phosphoric acid. Both the pyro- and the meta-acids readily take on water, and are changed back to the ortho acid.

The salts of arsenic acid are called arsenates.

As with orthophosphoric acid, mono-, di-, and trimetallic salts are known: NaH_2AsO_4, Na_2HAsO_4 and Na_3AsO_4.

The arsenates of the alkalies are soluble in water; the others are insoluble in water but easily soluble in acids.

Reactions in the Wet Way

1. **Hydrogen Sulfide** on being passed into a cold solution of an arsenate in 0.3-normal acid does not cause any precipitation until after a long time, when arsenic trisulfide is formed. If the *cold* solution contains a *large excess* of concentrated *hydrochloric acid*, the arsenic is precipitated as pentasulfide. If hydrogen sulfide is passed into a hot solution of an arsenate in concentrated hydrochloric acid, a mixture of arsenic trisulfide and pentasulfide is formed.

This behavior is very interesting, but the relations involved are quite complicated. The solubility products of both arsenic trisulfide and arsenic pentasulfide are extremely small, and it requires but a small quantity of either As^{+++} or As^{+++++} ions to reach this value even with the sulfur ions from slightly ionized hydrogen sulfide. A cold solution of an arsenate in 0.3-normal hydrochloric acid contains no appreciable quantity of As^{+++++} cations. Arsenic acid is of approximately the same strength as phosphoric acid and it is only in the presence of a very large excess of an acid, such as hydrochloric acid, that the ionization of the first hydrogen acid is repressed to a marked degree. In the presence of concentrated hydrochloric acid, however, it is reasonable to assume that a small quantity of As^{+++++} cations are present. These react with hydrogen sulfide to form the very insoluble pentasulfide,

$$H_3AsO_4 + 5\,H^+ \rightarrow 4\,H_2O + As^{+++++};\quad 2\,As^{+++++} + 5\,H_2S \rightarrow As_2S_5 + 10\,H^+.$$

The arsenic sulfide is so insoluble that the effect of the acid is, on the whole, favorable; it favors the formation of As^{+++++} cations and it prevents the formation of colloidal solutions of As_2S_5.

Hydrogen sulfide is absorbed by a cold solution of an arsenate in dilute acid to a greater extent than can be accounted for by the solubility of hydrogen sulfide in water. Soluble thioarsenates are formed:

$$H_3AsO_4 + H_2S \rightarrow H_3AsO_3S + H_2O.$$

Hydrogen sulfide also exerts a reducing effect upon the arsenate. This reduction takes place very slowly in the cold, but more rapidly if the temperature of the solution is raised or if the concentration of the H^+ is increased (cf. p. 242).

$$H_3AsO_4 + 3\,H^+ + H_2S^{--} \rightarrow As^{+++} + 4\,H_2O + S; \quad 2\,As^{+++} + 3\,H_2S \rightarrow As_2S_3 + 6\,H^+.$$

As soon as the solution contains an appreciable quantity of either As^{+++++} or As^{+++} ions, the precipitation of the corresponding sulfide at once takes place. The temperature of the solution and the concentration of the acid are exceedingly important factors in the precipitation of arsenic by means of hydrogen sulfide. The pentasulfide is the more insoluble of the two sulfides.

To precipitate the arsenic quickly by hydrogen sulfide from a solution of an arsenate, without employing considerable hydrochloric acid, it is only necessary to reduce the arsenic acid by boiling with sulfurous acid, to boil off the excess of the latter, and then to conduct hydrogen sulfide into the solution, whereby a precipitate of arsenious sulfide is at once formed.

Arsenic pentasulfide is insoluble in boiling concentrated hydrochloric acid, but, like the trisulfide, it is readily soluble in alkalies, ammonium carbonate, and alkali sulfides:

$$\mathbf{As_2S_5} + 6\,OH^- = 3\,H_2O + AsS_4^{---} + AsO_3S^{---};$$

$$\mathbf{As_2S_5} + 3\,CO_3^{--} = 3\,CO_2\uparrow + AsS_4^{---} + AsO_3S^{---};$$

$$\mathbf{As_2S_5} + 3\,S^{--} = 2\,AsS_4^{---}.$$

By acidifying these solutions, arsenic pentasulfide is reprecipitated:

$$2\,AsS_4^{---} + 6\,H^+ \rightarrow 3\,H_2S\uparrow + \mathbf{As_2S_5},$$

$$AsS_4^{---} + AsO_3S^{---} + 6\,H^+ \rightarrow 3\,H_2O + \mathbf{As_2S_5}.$$

Arsenic pentasulfide is oxidized by fuming nitric acid to sulfuric and arsenic acids; also by ammoniacal hydrogen peroxide and by hydrochloric acid and potassium chlorate:

$$\mathbf{As_2S_5} + 40\,HNO_3 \rightarrow 2\,H_3AsO_4 + 5\,H_2SO_4 + 40\,NO_2\uparrow + 12\,H_2O,$$

$$\mathbf{As_2S_5} + 20\,H_2O_2 + 16\,OH^- = 28\,H_2O + 5\,SO_4^{--} + 2\,AsO_4^{---},$$

$$3\,\mathbf{As_2S_5} + 20\,HClO_3 + 24\,H_2O \rightarrow 20\,HCl + 6\,H_3AsO_4 + 15\,H_2SO_4$$

or

$$3\,\mathbf{As_2S_5} + 5\,HClO_3 + 9\,H_2O \rightarrow 5\,HCl + 6\,H_3AsO_4 + 15\,\mathbf{S}.$$

2. **Silver Nitrate** precipitates from neutral solutions *chocolate-brown* silver arsenate (difference from arsenious and phosphoric acids):

$$AsO_4^{---} + 3\,Ag^+ \rightarrow \mathbf{Ag_3AsO_4},$$

soluble in acids and in ammonia.

3. ***Magnesium Chloride*** *precipitates, in the presence of ammonia and ammonium chloride, a white, crystalline precipitate of magnesium ammonium arsenate:*

$$AsO_4^{---} + Mg^{++} + NH_4^+ \rightarrow \mathbf{MgNH_4AsO_4}.$$

This precipitate is insoluble in dilute ammonia and is used for the quantitative determination of arsenic. By ignition it is changed into magnesium pyroarsenate:

$$2\,\mathbf{MgNH_4AsO_4} = H_2O\uparrow + 2\,NH_3\uparrow + \mathbf{Mg_2As_2O_7}.$$

4. **Ammonium Molybdate,** added in considerable excess to a boiling nitric acid solution, precipitates yellow, crystalline ammonium arsenomolybdate:

$$AsO_4^{---} + 3\,NH_4^+ + 12\,MoO_4^{--} + 24\,H^+ \rightarrow 12\,H_2O + \mathbf{(NH_4)_3AsO_4 \cdot 12\,MoO_3}.$$

This precipitate, like that of the corresponding molybdenum compound with phosphoric acid, is insoluble in dilute nitric acid solution containing ammonium nitrate, but is readily soluble in ammonia or caustic alkali solutions:

$$\mathbf{(NH_4)_3AsO_4 \cdot 12\,MoO_3} + 24\,OH^- \rightarrow 12\,H_2O + 3\,NH_4^+ + AsO_4^{---} + 12\,MoO_4^{--}.$$

The yellow precipitate is also soluble in a solution containing an alkali arsenate; complex anions containing more arsenic are formed and the ammonium salts of these complex ions are soluble in nitric acid. Consequently a large excess of ammonium molybdate should be used if it is desired to precipitate arsenic acid.

As we shall see later, phosphoric acid behaves similarly toward magnesium salts and ammonium molybdate. If, therefore, phosphoric acid and arsenic are both present, it is necessary to precipitate first the arsenic with hydrogen sulfide, filter, and oxidize the precipitated arsenic sulfide to arsenic acid with fuming nitric acid. In such a solution a precipitate produced by means of ammonium molybdate or magnesium chloride must be caused by arsenic acid. In the same way a precipitate produced *in the filtrate* from the hydrogen sulfide precipitate must be caused by phosphoric acid. This is safer than to depend upon the fact that the ammonium phosphomolybdate forms more readily at lower temperatures (60°) than does the corresponding arsenic compound.

5. **Potassium Iodide,** in a solution strongly acid with hydrochloric acid, reduces a solution of an arsenate with liberation of iodine (cf. p. 242);

$$H_3AsO_4 + 5\,H^+ + 2\,I^- \rightarrow As^{+++} + 4\,H_2O + I_2.$$

The reaction takes place quantitatively if the iodine is removed by adding sodium thiosulphate.

6. **Concentrated Hydrochloric Acid** and **Ferrous Chloride** cause the formation of volatile arsenious chloride:

$$H_3AsO_4 + 2\,FeCl_2 + 5\,HCl \rightarrow AsCl_3\uparrow + 2\,FeCl_3 + 4\,H_2O.$$

Any other soluble ferrous salt may be used and other reducing agents such as cuprous chloride, potassium iodide, potassium bromide or even hydrogen sulfide. After this treatment, all the arsenic may be removed by distilling in a stream of hydrogen chloride.

7. **Ammonium Thioacetate** and **Sodium Thiosulfate** cause the same precipitation as with arsenious salts.

8. **Cupric Sulfate** does not give a precipitate with arsenic acid solutions unless a little alkali hydroxide is added and then bluish green cupric arsenate is formed which becomes a beautiful light blue on adding more alkali but does not dissolve.

C. Reactions which May be Obtained with All Arsenic Compounds

1. **The Marsh Test for Arsenic.** — All compounds containing arsenic may be reduced, in acid solution, by means of metallic zinc to arsine, AsH_3:

$$AsO_3^{---} + 3\,Zn + 9\,H^+ \rightarrow 3\,Zn^{++} + 3\,H_2O + AsH_3\uparrow.$$

$$AsO_4^{---} + 4\,Zn + 11\,H^+ \rightarrow 4\,Zn^{++} + 4\,H_2O + AsH_3\uparrow.$$

$$As^{+++} + 3\,Zn + 3\,H^+ \rightarrow 3\,Zn^{++} + AsH_3\uparrow.$$

The sulfides are reduced very slowly, but the oxides are reduced quickly even at ordinary temperatures.

This *very* poisonous arsine possesses a property which enables us to detect with certainty the merest trace of arsenic — as little as 0.0007 milligram As. By conducting the gas through a heated glass tube filled with hydrogen, it is decomposed into hydrogen and metallic arsenic; and the latter is deposited as a brownish-black mirror on the sides of the glass tube, just beyond the place where it was heated.

This test is extremely sensitive, and must be made with caution, as almost all reagents, especially commercial zinc and sulfuric acid, are likely to contain traces of arsenic. In case these are used without previous testing, arsenic is likely to be found even although it may not have been present in the substance itself.

The Marsh test is particularly useful for detecting the presence of very small amounts of arsenic which could not be found by any of the previously mentioned reactions. In cases of poisoning and for detecting the presence of arsenic in wall-papers, this test, or a modification of it, is always used; we will, therefore, discuss it in detail.

Formation and Properties of Arsine

(*a*) *Formation.* — Arseniuretted hydrogen, or arsine, is produced, as above mentioned, by the reduction of compounds containing arsenic. For accomplishing the reduction, pure zinc and pure sulfuric acid should be used. If other metals and other acids are used (e.g., tin and hydrochloric acid, iron and sulfuric acid) the arsenic compound will be reduced; but if iron is used, a part of the arsenic is changed to solid arseniuretted hydrogen, which remains in the flask and consequently escapes detection. If tin and hydrochloric acid are used, a high temperature is necessary in order to accomplish the reduction,* while with zinc and sulfuric acid the reaction takes place readily at the ordinary temperature. Chemically-pure zinc dissolves with difficulty in chemically-pure sulfuric acid, so that it is well to activate the zinc by the addition of a little foreign metal. The addition of a drop of chloroplatinic acid causes at first a more rapid evolution of hydrogen, but the reaction soon slows down and is not accelerated by the addition of more chloroplatinic acid. Moreover, the addition of chloroplatinic acid has the disadvantage of causing considerable arsenic to be held back by the platinum; less than 0.005 mgm. of As_2O_3 cannot be detected in this way.† Much better results are obtained by using an alloy of zinc and platinum. Thus F. Hefti ‡ found that zinc alloyed with 10 per cent platinum caused a more uniform evolution of hydrogen and that the formation of arsine was accelerated, while less arsenic was retained by the platinum. With this alloy, 0.0005 mgm. of As_2O_3 can be detected with certainty. The best activating agent, however, is copper in the form of a zinc-copper alloy prepared as follows: Melt 20 gms. of the purest zinc in a small Hessian crucible, stir a very little pure copper into the molten zinc with the aid of a stick of zinc. Pour the molten metal into water, keeping as much as possible of the oxide back in the crucible. With this alloy and 15 per cent sulfuric acid, a steady, continuous current of gas is obtained and it is possible to detect with certainty as little as 0.00025 mgm. of As_2O_3.

Arsenic, arsenious oxide, arsenic pentoxide, and arsenic trisulfide are readily reduced in alkaline solution by sodium amalgam, aluminium, or Devarda's alloy and caustic potash. The reduction takes place quickly, and the arsine may be detected by the Gutzeit reaction (cf. p. 253). The presence of organic matter in solution hinders the reaction; 3 cc. of urine in which 1 mgm. of As_2O_3 was dissolved showed no trace of arsine after treating for hours with Devarda's alloy and caustic potash solution. In such cases the organic substance must be decomposed before testing for arsenic. (Cf. pp. 137 and 161.)

Arsine is also obtained by dissolving many arsenides in hydrochloric or sulfuric acid:

$$Zn_3As_2 + 6\,HCl = 3\,ZnCl_2 + 2\,AsH_3\uparrow.$$

Arsenide of iron is attacked by acids only with difficulty, except when an excess of iron is present; solid and gaseous arsenic hydrides are formed. Consequently iron

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* Thus VANINO, working at ordinary temperatures, could not detect less than 0.002 gm. of As_2O_3 by means of tin and hydrochloric acid, and where chloroplatinic acid was added, less than 0.1 mgm. of As_2O_3 could not be found. *Z. angew. Chem.*, **1902**, 82.

† BERNSTEIN, Inaug.-Dissert., Rostock, 1870.

‡ Inaug.-Dissert., Zurich, 1907.

sulfide containing arsenic, on treatment with acids, always yields hydrogen sulfide contaminated with arsine.*

Arsenites can also be reduced to arsine by the action of the electric current. It is possible to distinguish between an arsenite and an arsenate in this way.

Certain microbes, namely, *Penicillium brevicaule*, when provided with nutriment containing only traces of arsenic, have the power of forming volatile arsenic compound of a garlic odor, and this may be used as an extremely sensitive test for arsenic.

(*b*) *Properties.* — Arsine is a colorless, unpleasant-smelling, extremely poisonous gas, which, on being heated away from the air, is decomposed into arsenic and hydrogen:

$$4\,AsH_3 = As_4 + 6\,H_2.$$

By heating in the air, it is oxidized to water and arsenic trioxide. Solid iodine changes it to arsenious iodide and hydriodic acid:

$$AsH_3 + 3\,I_2 = AsI_3 + 3\,HI.$$

This reaction takes place on conducting arsine over solid iodine. *This property serves to free hydrogen sulfide from arsine*, as hydrogen sulfide does not act upon solid iodine, but only upon aqueous iodine solutions. Arsine is not attacked by hydrogen sulfide at ordinary temperatures, but at 230° C. sulfide of arsenic and hydrogen are formed.

Arsine is a strong reducing agent: silver salts are reduced to metal (see p. 253).

Directions for Performing the Berzelius-Marsh Test

The apparatus devised by G. Lockemann,† shown in Fig. 20, may be used to advantage.

In the flask *K*, of 100 to 150 cc. capacity, place 3 or 4 gms. of zinc alloyed with copper (cf. p. 248) and about 20 cc. of 4-normal sulphuric acid free from arsenic. A steady stream of hydrogen is at once evolved, and in twenty minutes the air will be entirely driven out of the apparatus. When, at the end of about twenty minutes, the gas escaping at *b* is found to be pure (by collecting a little in a small tube and holding it near a flame; it should light without a sharp explosion), light the hydrogen at *b*.‡ The flame should be about 2 or 3 mm. high and should remain so during the entire experiment; if it becomes higher, cool the solution in *K* by placing the flask in cold water, and, conversely, if the flame is too low add a little more sulphuric acid or place the flask in warm water.

First of all, test the zinc and sulphuric acid to see that they are free from arsenic. Heat the hard-glass tube at *B* just before the restriction in the tube, which is 5 mm. long and 1.5–2 mm. wide. If at the end of twenty minutes there is no arsenic mirror formed in this capillary, the reagents are free from arsenic.

Transfer the sulfuric acid solution to be tested for arsenic, and which must be free from organic substances, sulfides, chlorides, nitrates, or other oxidizing agent,

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* (*Chem. Zentralbl.*, **1902**, I, p. 1245.)

† *Z. angew. Chem.*, **1905**, pp. 427 and 491.

‡ A safe way to light the flame is to fill a small tube with the escaping gas, light it, and bring it slowly to the end of the tube *b*. If the gas is pure the hydrogen in the small tube will burn quietly for some little time. If impure, there will be none left in the small tube after it is exploded and this will not light the escaping gas at *b*.

to the graduated funnel T, and add it little by little to the flask K without in any way interrupting the current of hydrogen. Just before adding the solution to the flask, light the two burners at A and thereby heat the glass tube to dull redness. The gas as it escapes from the flask K passes through the drying-tube C containing granular calcium chloride, and then into the tube A, where any arsine is quantitatively decomposed into arsenic and hydrogen. The arsenic is deposited on the cold walls of the capillary. Cool the end of the capillary, in order to form a sharply defined mirror, by winding around it a piece of wicking, as shown in Fig. 20, and allowing water to drop upon it from the dish W during the experiment.

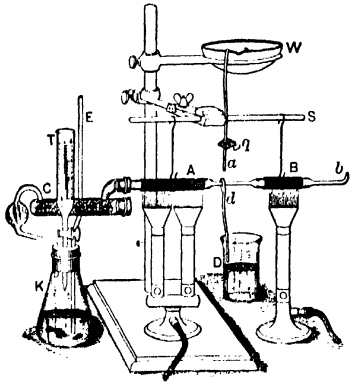

FIG. 20

All the arsenic will be deposited at the end of an hour, and by comparing the mirror with a series of standards the amount can be estimated accurately (see page 252).

Remark. — If the tube A is not heated at all, but the gas ignited at b as above described, the arsenic may be deposited upon a cold porcelain dish by holding the dish in the flame. The deposit is readily soluble in sodium hypochlorite solution (difference from antimony). In this form the test was used by James Marsh in 1836.

Confirmatory Test. — In the small glass tube open at both ends (see Fig. 21) the arsenic mirror is found. Hold the tube in an inclined position and heat it by means of a small flame whereby the arsenic is changed to arsenic trioxide, giving off the characteristic garlic odor, which can be detected at the upper end of the tube if only 0.01 mgm. of arsenic trioxide is formed. After the tube is cooled, the arsenic trioxide is to be found at a in the form of small glistening octahedrons, which can be seen with the magnifying glass or often with the naked eye.

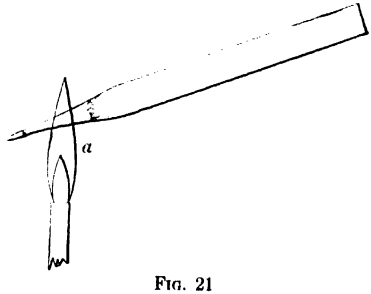

FIG. 21

These three facts — formation of the mirror, the garlic odor, and the octahedrons — suffice to prove the presence of arsenic; but the more proofs we have, the more certain we are of the accuracy of the result. If the octahedrons have been recognized, seal the capillary end of the tube with a flame, and introduce 1 to 2 drops of pure, concentrated hydrochloric acid into the tube with the help of a dropper, and move the tube so that the arsenic trioxide is moistened by the acid; then add 6 to 10 drops of distilled water and pass hydrogen sulfide into the tube, whereby yellow arsenious sulfide is formed.

The hydrogen sulfide required may be generated from a solution of sodium sulfide by allowing it to flow into dilute sulfuric acid, as illustrated in Fig. 22. The upper part of the test-tube contains a wad of cotton wool, which prevents any of the solution in the tube from being mechanically carried over into the tube containing the arsenic.

As an example of the practical application of this delicate test, the method to be employed in the detection of arsenic in wall-papers, etc. will be described. The amount of arsenic contained in wall-papers is usually so small that weighing the mirror produced would not be accurate.* It is best, therefore, to prepare a number of mirrors from known amounts of arsenic, to establish a scale for determining how much is contained in the given wall-paper or fabric.†

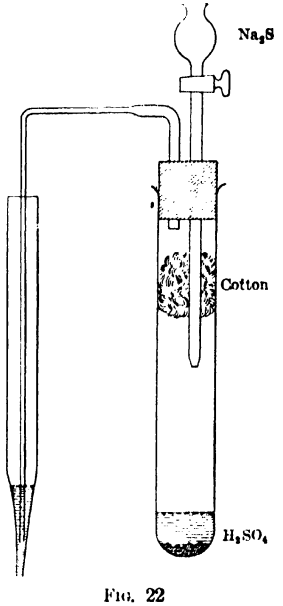

FIG. 22

First of all, the arsenic must be extracted completely from the paper, and to this end it is necessary to decompose the organic material, which is accomplished preferably as follows:

Decomposition of Organic Material

Take exactly one square decimeter (100 sq. cm.) of wall-paper, roll it into a cylinder and push it down into a tube closed at one end, such as is used for the Carius determination of the halogens (see Volume II of this book). Add 2 cc. of pure, fuming sulfuric acid (25 per cent oleum) through a long-stemmed funnel. Then pour 3 or 4 cc. of fuming nitric acid into a small test-tube and carefully allow the latter to slip down the sides of the Carius tube so that the two acids do not come in contact with one another. At the open end of the tube draw out the glass to form a strong capillary and seal the end as described in Volume II. Cover the tube with asbestos paper and slowly heat it inside a strong iron tube, in the furnace used for Carius tubes, to a temperature of about 230° and keep it at this temperature for an hour and a half. Allow the tube to cool and then withdraw it from the iron protective tube, by means of a wire previously fastened to it, until the capillary projects a little; heat this with a Bunsen flame. As soon as the glass becomes soft the pressure on the inside of the tube blows out a hole through which gas escapes until the pressure is the same inside the tube as without. Break off the point of the tube and rinse the contents of the tube and of the tip into a porce-

* In Massachusetts, the law permits the presence of 0.1 mgm. per square decimeter in wall-paper, but only 0.01 mgm. per square decimeter in wearing apparel. In most cases it is merely necessary to determine whether the legal limit is exceeded.

† C. R. SANGER, *Amer. Acad. of Arts and Sciences*, **26**, 24.

lain evaporating dish. The colorless solution * thus obtained will contain all the arsenic in the form of arsenic acid. Evaporate the solution till fumes of sulfuric acid are evolved thickly, and then, after cooling, add 15 cc. of water and pour the liquid into the funnel T of Fig. 20, rinsing the dish twice with 3 cc. portions of water. After mixing the liquid in T by means of a small stirring rod, make a note of the total volume of the liquid.† During this operation, the Marsh apparatus should be made ready for the test.

When the apparatus is ready, add a few drops of the well-mixed solution through T to the reduction flask K. If no mirror appears within three or four minutes add one-eighth to one-quarter of the filtrate little by little; and if no mirror appears after five minutes, the whole filtrate. The whole filtrate is not added at once, because if too strong a mirror is obtained, it is much more difficult to estimate the amount of arsenic present. After twenty-five minutes all the arsenic will be deposited if not more than 0.05 mg. of arsenic is in solution. If a mirror of sufficient density was obtained in fifteen minutes from only a fraction of the whole solution, no more should be added, but the operation should be continued for ten minutes more, the flame extinguished, and the tube allowed to cool while hydrogen continues to pass through it. The mirror is then compared with the scale, and the remaining part of the filtrate is weighed in order to determine how much was used for the test.

If sufficient material is at hand, a duplicate experiment should be made with a new tube and a new sample. The results of a few such determinations are given in the following table:

Sq. cm. of Paper Used.	Weight of Extract.	Wt. of Extract Taken.	Weight of Mirror.	Total Weight of As_2O_3 in Extract.	Wt. As_2O_3 in mgm. per sq. meter.
100	31.63	31.63	0	0	0
100	30.11	10.23	0.015	0.044	4.4
...	.....	9.87	0.013	0.0399	3.99
100	28.72	8.32	0.045	0.155	15.5
...	.....	7.53	0.042	0.163	16.3
50	30.22	2.64	0.015	0.172	34.4
...	.....	3.22	0.020	0.187	37.4

The comparison of the mirrors is best made in transmitted light. The normal mirrors are prepared as follows: Dissolve 1 gm. of pure, sublimed arsenic trioxide in a little sodium carbonate solution, acidify with dilute sulfuric acid, and dilute to a liter. Take 10 cc. of this solution, of which 1 cc. contains 1 mg. of As_2O_3, and again dilute to a liter; in this way a solution is obtained of which 1 cc. contains exactly 0.01 mg. of As_2O_3. Measure out 1 cc., 2 cc., 3 cc., 4 cc., and 5 cc. of the solution and introduce each portion separately into the Marsh apparatus, and prepare the corresponding mirrors in different tubes. It is best to prepare two tubes from each amount of arsenic, as the mirrors are not always the same. These mirrors may be kept in the dark for some time; but on exposure to the light they fade perceptibly. Mirrors which are sealed up with hydrogen do not keep as well.

* If the paper contained iron or aluminium compounds, the anhydrous sulfates are formed. These dissolve by heating with water. The above method is the best and cleanest for decomposing organic material.

† Instead of measuring the liquid it may be weighed.

Testing Urine, Blood, Milk, Beer, etc., for Arsenic

Evaporate 100 cc. of the liquid in question to dryness in a porcelain dish. By means of a spatula introduce the residue as completely as possible into a tube, such as is used for the Carius determination (Vol. II), and add 4 cc. of a 25 per cent oleum. In order to transfer the rest of the residue to the tube, pour 2 cc. of fuming nitric acid into the dish and after wetting all the sides of the dish, transfer the acid to a small test-tube. Repeat this operation twice more and then allow the small test-tube to slip into the Carius tube. Draw out a capillary at the open end of the tube and seal it by the flame. Heat the tube in the Carius furnace for one hour at 160°. After cooling, open the point of the tube with the usual precautions (p. 251), and release the pressure. Seal the tube again and heat for half an hour to an hour at 230°. The operation is then continued as described above.

With urine a somewhat different procedure is followed. Evaporate the liquid not quite to dryness, but to sirupy consistency; spread the sirup upon a porcelain boat and allow it to slip into the Carius tube. The rest of the process is carried out as before.

2. **The Gutzeit Test for Arsenic** depends upon the behavior of arsine toward a 50 per cent. solution of silver nitrate (according to Eidenbenz, a crystal of solid silver nitrate should be used). The silver nitrate is at first colored yellow and then black, the following reactions taking place:

$$(a)\quad 6\,AgNO_3 + AsH_3 = \underbrace{AsAg_3 \cdot 3\,AgNO_3}_{\text{Yellow}} + 3\,HNO_3.$$

$$(b)\quad AsAg_3 \cdot 3\,AgNO_3 + 3\,HOH = H_3AsO_3 + 3\,HNO_3 + 6\,Ag.$$

The test is carried out as follows: Place a little of the substance in a small test-tube, Fig. 23, add a few grains of zinc and a little dilute sulfuric acid, and place a wad of cotton near the top of the tube as a filter. Over the mouth of the tube place a piece of filter-paper with a crystal of silver nitrate on top.

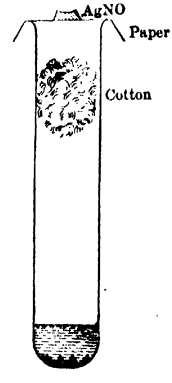

FIG. 23

If arsenic is present, the silver nitrate is at first turned yellow, but it becomes black very quickly.

This reaction is often used for quickly testing commercial acid for arsenic, but it is not as reliable as the Bettendorff test (p. 243), because phosphine * and stibine give a similar reaction with silver nitrate, while they are not reduced by stannous chloride.

If arsine is allowed to act upon a dilute solution of silver nitrate, the yellow compound $AsAg_3 \cdot 3\,AgNO_3$ is not formed, for it is immediately decomposed hydrolytically, according to the equation

$$AsH_3 + 6\,AgNO_3 + 3\,HOH = 6\,HNO_3 + H_3AsO_3 + 6\,Ag.$$

If the precipitated silver is filtered off, and ammonia then poured on top of the filtrate, the neutral zone will appear yellow owing to the formation of silver arsenite.

* Commercial zinc often contains a small quantity of phosphorus.

This reaction never takes place quite quantitatively; the deposited silver invariably contains a little silver arsenide, Ag_3As.

If the silver solution is made ammoniacal, it is true that all the arsine will be absorbed, but the deposited silver still contains a little arsenic and the solution a small quantity of ammonium arsenate. If, however, the ammoniacal solution containing the silver nitrate and ammonium arsenite is heated to boiling, then the arsenite is oxidized quantitatively to arsenate with deposition of silver.*

$$2\,Ag^+ + AsO_3^{---} + OH^- \rightarrow HAsO_4^{--} + 2\,\mathbf{Ag}.$$

Under these conditions eight atoms of silver are deposited from each original molecule of arsine

$$AsH_3 + 8\,Ag^+ + 11\,OH^- \rightarrow AsO_4^{---} + 7\,H_2O + 8\,\mathbf{Ag}.$$

If the deposited silver is filtered off and the filtrate carefully neutralized with nitric acid, a brown precipitate of silver arsenate is formed.

Somewhat less sensitive than the original Gutzeit test, although very satisfactory, is the modification recommended by Flückiger † and Lehmann.‡

Instead of allowing the arsine to act upon silver nitrate, bring it into contact with mercuric chloride § paper, which is turned yellow by a little arsine and reddish brown by considerable arsine.‖

The exact composition of these compounds is not known definitely. Possibly $As(HgCl)_3$ is formed first; and then, by further action of AsH_3, $AsH(HgCl)_2$ and As_2Hg_3 are formed.¶

$$AsH_3 + 3\,HgCl_2 \rightarrow 3\,HCl + \mathbf{As(HgCl)_3},$$

$$2\,\mathbf{As(HgCl)_3} + AsH_3 \rightarrow 3\,\mathbf{AsH(HgCl)_2},$$

$$\mathbf{As(HgCl)_3} + AsH_3 \rightarrow 3\,HCl + \mathbf{As_2Hg_3}.$$

These arsenic compounds are characterized by their insolubility in 80 per cent alcohol.

Stibine gives no reaction in this test when little of it is present, but the presence of somewhat more of it causes the formation of a brown spot which is soluble in alcohol. If, however, arsenic and antimony are both present, the former is recognized by cutting out the spot from the rest of the filter-paper and placing it in 80 per cent alcohol, whereby the brown spot due to the antimony is removed in a short time and the yellow arsenic spot appears plainly. When considerable antimony is present, the test fails; a gray-black spot is produced which does not disappear on treatment with alcohol.

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* Cf. Reckleben, Lockemann, and Eckhardt, *Z. anal. Chem.*, **1907**, 671.

† *Arch. Pharm.* [3], **1889**, 27.

‡ *Pharm. Ztg. Berlin*, **1892**, 36.

§ To prepare the mercuric chloride paper moisten some filter-paper with an alcoholic solution of mercuric chloride, allow the alcohol to evaporate and repeat the process four or five times.

‖ August Gotthelf, *J. Soc. Chem. Ind.*, **22**, 191 (1903).

¶ Besides the above compounds, $AsH_2(HgCl)$ and As_2Hg_3 are said to exist. Cf. Partheil, *Arch. Pharm.*, **237**, 121.

3. **The Reinsch Test** is very easy to make, but it is not as sensitive as the tests just mentioned. It depends upon the fact that when a strip of polished copper foil is added to a solution of arsenious acid, the copper is colored gray owing to the deposition of Cu_5As_2 on the copper.

From concentrated solutions the arsenic separates out in the cold, but from dilute solutions only on warming. If considerable arsenic is present, the gray copper arsenide drops off from the copper. Antimony is also precipitated on copper from its solutions, so that the deposit must be tested for arsenic in the dry way. Arsenic acid is also reduced by copper, but only on warming.

The Reinsch test is often used in testing wall-papers for arsenic. The pieces of paper are treated with a little hydrochloric acid (1 : 2), a piece of copper foil added, and warmed. A gray deposit on the copper indicates the presence of arsenic.

To confirm this test, the piece of gray copper foil is placed in a tube of difficultly fusible glass and heated in a stream of hydrogen gas; an arsenic mirror is produced which can be tested as described on p. 250.

Detection of Arsenic in Human Organs

To detect small quantities of arsenic present in the organs of persons who have probably died from poisoning, it is necessary in the first place to destroy all the organic tissue; this may be accomplished by the action of sulfuric and nitric acids.* Place 200 g. of the organ, 200 cc. of concentrated nitric acid and 5 cc. of 2 per cent permanganate solution in a 2-liter flask and heat until foaming ceases. Then transfer the solution to a 1-liter flask, rinsing out the larger flask with 100 cc. of concentrated nitric acid and 100 cc. of water. Boil four hours, or until the solution is reduced to 80 cc. in volume. Add 100 cc. of concentrated sulfuric acid and evaporate till fumes of sulfuric acid are evolved. Cool, add 2 or 3 cc. of concentrated nitric acid and again heat until white fumes are evolved and repeat this treatment with nitric acid about six times. Then, when all the nitric acid has been expelled, cool, dilute with 100 cc. of water and test the solution by the Marsh test.

To determine the *quantity* of arsenic present, transfer the solution to a distilling flask, add 20 cc. of concentrated sulfuric acid, 50 gms. of sodium chloride, 1 gm. of potassium chloride and 10 gms. of ferrous sulfate crystals. Distill into a flask containing 50 gms. of sodium bicarbonate and 100 cc. of water until all the solid bicarbonate dissolves. Titrate the sodium arsenite solution thus obtained with iodine as described in Vol. II. A blank experiment should be made with all the reagents to make sure that they are free from arsenic.

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* Cf. GAUTIER, *Bull. soc. chim. Paris*, **25**, 252 (1875); CHITTENDEN and DONALDSON, *Am. Chem. J.*, **11**, 236 (1880–1); JOACHIMOGHI, *Arch. exp. Path. Pharm.*, **78**, 1–16 (1914).

Reactions in the Dry Way

Metallic arsenic burns, giving off a garlic odor. Mixed with sodium carbonate and heated on charcoal, all arsenic compounds give this odor.

Oxygen compounds of arsenic are easily reduced to metal in the upper reducing flame. On holding a porcelain dish (glazed on the outside and filled with water) directly over the sample, the arsenic vapors are condensed on the dish, forming a brownish-black coating which is soluble in sodium hypochlorite solution, disappearing instantly, the arsenic being oxidized to arsenic acid:

$$As_4 + 10\ NaOCl + 6\ H_2O = 10\ NaCl + 4\ H_3AsO_4.$$

If the porcelain dish is not held closely above the reducing flame, but above the upper oxidizing flame, the arsenic vapors are burned with a bluish flame to white arsenious oxide which deposits on the dish.

If this deposit is moistened with silver nitrate, and ammonia vapors blown upon it, a yellow coloration due to Ag_3AsO_3 is formed, which disappears if more ammonia is allowed to act upon it (difference from antimony):

$$As_2O_3 + 6\ AgNO_3 + 3\ H_2O = 2\ Ag_3AsO_3 + 6\ HNO_3.$$

The ammonia serves to neutralize the nitric acid formed by the reaction, but the precipitate dissolves in excess of ammonia as well as in nitric acid.

The microchemical method of Hartwich and Toggenburg * is often useful when the arsenic is present as trioxide. Prepare a glass cylinder about 12 mm. in diameter and 10 mm. in height and make sure that both the upper and lower edges are smooth. Place this cylinder upon a small watch-glass and pour into it a little of the substance to be tested, well mixed with ignited sand. Cover the cylinder with a flat glass slide about 50 mm. square. Heat the watch-glass very carefully with the flame from a small burner; the flame should not be over 5 mm. high and 30 to 40 mm. below the watch-glass. After heating ten or fifteen minutes, allow to cool slowly and finally examine the bottom surface of the glass slide. If arsenic is present as trioxide, it will have sublimed and the vapors will have condensed, upon the slide for the most part, in the form of beautiful octahedrons, the shape of which is very distinct when viewed under the microscope. These crystals are visible when only 0.01 mg. of arsenic is present. The sublimate may be identified further by the silver reaction.

Arsenic trioxide or trisulfide is readily reduced to metallic arsenic by fusion with a mixture of 3 parts sodium carbonate and 1 part potassium cyanide. With the oxide the cyanide is changed to cyanate but with

* *Schweiz. Wochenschrift, für Chem. u. Pharm.* **1909**, No. 52, p. 1.

the sulfide some thiocyanate is formed. The reaction succeeds with arsenites provided the cation is not reduced by potassium cyanide or yields an arsenide which is easily decomposed by heating. This reaction is recommended by Fresenius and Babo as most suitable for detecting the presence of small quantities of arsenic. They recommend the following procedure:

Triturate the perfectly dry arsenic compound with 3 times as much dry potassium cyanide and 9 times as much sodium carbonate in a mortar which has been warmed. To avoid contact of the fusion mixture with glass, which is likely to contain arsenic, place the mixture in a small porcelain boat and introduce the boat into a piece of glass tubing which is drawn out into a capillary at one end. Connect the other end of the tubing with a carbon dioxide generator, interposing a wash bottle with a little sulfuric acid to dry the carbon dioxide. The porcelain boat should rest in the middle of the glass tube. With a moderate stream of carbon dioxide passing through the apparatus, heat the whole length of the glass tube to remove all moisture, then shut off the flow of gas somewhat and heat the end of the tube where the constriction begins. When this is hot place another lamp under the porcelain boat and continue heating until all the arsenic is expelled. Most of it will condense in the narrow tubing but some may escape into the air and give a garlic odor. 0.01 mg. of arsenious acid will produce a visible mirror of arsenic.

ANTIMONY, Sb. At. Wt. 120.2

Sp. Gr. = 6.7–6.8. M. Pt. = 630° C. B. Pt. = about 1450° C.

Occurrence. — Antimony seldom occurs free in nature, although large amounts of the metal have been found recently in Australia. The most important compounds containing antimony are (as with arsenic) the sulfur compounds. Stibnite, Sb_2S_3, orthorhombic, is found in Japan in beautiful crystals. The occurrence of kermesite, Sb_2OS_2, is interesting, as this compound is often met with in analysis.

Of the oxygen compounds the dimorphous antimony trioxide is known as isometric senarmontite and orthorhombic valentinite. Antimony also occurs in many thio salts, of which the tribasic silver thioantimonite, or pyrargyrite, Ag_3SbS_3, may be mentioned.

Antimony is a silver-white, brittle metal. It burns readily in the air to antimony trioxide. The solvent for antimony is aqua regia, by which it is converted into the trichloride or pentachloride. Nitric acid attacks antimony, changing it into Sb_2O_4, which dissolves slightly in concentrated acid, but is insoluble in dilute acid. Antimony dissolves easily in a mixture of nitric and tartaric acids, and in a mixture of hydrochloric acid and bromine.

Antimony forms three oxides: antimony trioxide, Sb_2O_3; antimony pentoxide, Sb_2O_5; and antimony tetroxide, Sb_2O_4, which may be regarded as antimonous antimonate, and is a very indifferent sub-

stance chemically. Antimony trioxide as a rule shows basic properties, while antimony pentoxide has more the character of an acid anhydride.

A. Compounds of Antimony Trioxide

By burning the metal in the air, the trioxide is obtained, which on stronger ignition in the presence of air is changed to the inert Sb_2O_4.

The trioxide is dissolved by concentrated hydrochloric acid, forming antimony trichloride, a compound which (like bismuth chloride) is readily changed into a basic salt by the action of water, the decomposition of which depends upon the concentration of the reacting substances. Thus antimonyl chloride, SbOCl, is known, which is formed: according to the following equation:

$$SbCl_3 + H_2O \rightleftarrows 2\ HCl + \mathbf{SbOCl}.$$

In the presence of a large amount of water some oxide is also formed:

$$2\ \mathbf{SbOCl} + H_2O \rightleftarrows 2\ HCl + \mathbf{Sb_2O_3}.$$

A mixture of antimonyl chloride and antimony trioxide is known as "algarot" powder, $Sb_2O_3 \cdot 2\ SbOCl$.

By boiling with considerable water the oxide alone is obtained.

Antimony trioxide forms three hydroxides, which behave as very weak acids: orthoantimonous acid, H_3SbO_3; pyroantimonous acid, $H_4Sb_2O_5$; and the hypothetical metantimonous acid, $HSbO_2$.

Salts of the metantimonous acid are known, although the free acid itself has never been isolated. On boiling the oxide Sb_2O_3 with concentrated caustic soda or potash, it goes into solution, but on dilution with considerable hot water Sb_2O_3 separates out again. On filtering this off, tetragonal crystals of $NaSbO_2$ are deposited in the filtrate on cooling; they are, however, very unstable, and are decomposed by standing in the air into sodium carbonate and antimony trioxide. By dissolving antimony trioxide in strong alkali, the orthoantimonate is probably formed,

$$\mathbf{Sb_2O_3} + 6\ OH^- \rightarrow 2\ SbO_3^{---} + 3\ H_2O,$$

which is hydrolyzed on dilution into metantimonite and alkali hydroxide:

$$SbO_3^{---} + H_2O \rightarrow 2\ OH^- + SbO_2^-.$$

The latter is decomposed by more water into trioxide and alkali hydroxide; so that on adding to a solution of the trichloride either sodium hydroxide or carbonate, an almost quantitative precipitation of Sb_2O_3 will be obtained:

$$2\ SbCl_3 + 6\ NaOH = 6\ NaCl + 3\ H_2O + \mathbf{Sb_2O_3};$$

$$2\ SbCl_3 + 3\ Na_2CO_3 = 6\ NaCl + 3\ CO_2\uparrow + \mathbf{Sb_2O_3}.$$

Antimony oxychloride, SbOCl, contains the univalent group, SbO^+, which is known as the antimonyl group.

Antimony oxychloride, therefore, can be regarded as antimonyl chloride. Antimonyl nitrate $SbO(NO_3)$, is also known, and antimonyl sulfate, $(SbO)_2SO_4$. All these compounds are easily hydrolyzed into acid and oxide, so that they are rarely met with in the course of analysis, with the exception of antimonyl chloride.

The antimonyl compounds of certain organic acids (such as tartaric acid) are very much more stable.

On boiling antimony trioxide with a solution of potassium acid tartrate, it dissolves, forming the so-called "tartar emetic,"

$$2\ KHC_4H_4O_6 + Sb_2O_3 \rightarrow H_2O + 2\ K(SbO)C_4H_4O_6,$$

which is comparatively soluble in water. 100 cc. of water dissolve 5.3 gms. at 8.7°; 7.9 gms. at 21°; 12.2 gms. at 31°; 18.2 gms. at 50°, and 31.2 gms. at 75°.

Not only antimonyl oxide, Sb_2O_3, but all antimonyl compounds, form a complex anion with tartaric acid or with a tartrate; thus, antimonyl chloride dissolves in Rochelle salt, or in tartaric acid:

$$C_4H_4O_6^{--} + SbOCl \rightarrow Cl^- + [(SbO)C_4H_4O_6]^-;$$
$$H_2C_4H_4O_6 + SbOCl \rightarrow HCl + H[(SbO)C_4H_4O_6].$$

Tartar emetic, $K(SbO)C_4H_4O_6 \cdot \frac{1}{2}\ H_2O$, is the most important antimony compound of commerce. Consequently it will be worth while to say a few words with regard to its behavior toward acids.

If an aqueous solution of potassium antimonyl tartrate is treated with hydrochloric acid, a white precipitate of antimonyl chloride is formed,

$$K(SbO)C_4H_4O_6 + 2\ H^+ + Cl^- \rightarrow H_2C_4H_4O_6 + K^+ + SbOCl,$$

which readily dissolves in more hydrochloric acid,

$$SbOCl + 2\ HCl \rightleftarrows H_2O + SbCl_3,$$

but, on the addition of more water, it is reprecipitated, etc.

Sulfuric and nitric acids precipitate orthoantimonous acid from a solution of potassium antimonyl tartrate; for the antimonyl compound, which is at first formed, is immediately decomposed by water,

$$[(SbO)C_4H_4O_6]^- + H^+ + 2\ H_2O \rightarrow H_2C_4H_4O_6 + H_3SbO_3.$$

Reactions of Antimonous Compounds in the Wet Way

1. **Water** precipitates at first a basic salt which is changed into oxide by more water.

2. **Sodium Hydroxide, Ammonia,** and **Alkali Carbonates** precipitate the amorphous hydrated oxide.

3. **Hydrogen Sulfide** precipitates, from solutions which are not too acid, flocculent, orange-red antimony trisulfide:

$$2\,Sb^{+++} + 3\,H_2S \rightarrow 6\,H^+ + \mathbf{Sb_2S_3}.$$

As is indicated in the equation, the antimony trisulfide is in equilibrium with hydrogen ions; in 12-normal acid it is readily soluble (difference from arsenic). On the other hand, antimony sulfide is less soluble in acid than is tin sulfide and it can be precipitated from a solution which is normal in acid concentration. The trisulfides of both tin and antimony are somewhat more soluble than the pentasulfides. If a solution of antimony in concentrated hydrochloride is to be treated with hydrogen sulfide and the solution is first diluted, a precipitate of SbOCl is likely to form. This does no harm, as hydrogen sulfide will change antimonyl chloride into the less soluble trisulfide. If it is desired to precipitate the sulfide without any formation of antimonyl chloride, the solution should be saturated with hydrogen sulfide before it is diluted, then diluted and again saturated with hydrogen sulfide.

By heating orange antimony sulfide in an inert atmosphere (CO_2) it is changed to black antimony trisulfide. By roasting in the air, antimony tetroxide, Sb_2O_4, is formed. Heated with sodium nitrate, a mixture of sodium sulfate and pyroantimonate is formed. Heated in chlorine, or with a mixture of 5 parts ammonium chloride and 1 part ammonium nitrate, the antimony is changed to chloride which can be volatilized though less readily than in the case of the corresponding arsenic compound.

Antimony trisulfide is soluble in ammonium sulfide, forming a soluble thio salt:

$$\mathbf{Sb_2S_3} + 3\,S^{--} \rightarrow 2\,[SbS_3]^{---}$$

The triammonium salt has never been isolated, the mono salt, NH_4SbS_2, alone being known in the solid state. In solution, however, particularly in the presence of considerable ammonium sulfide, the SbS_3^{---} ion is probably present.

If yellow ammonium sulfide is employed, ammonium salts of thioantimonic acid are obtained:

$$\mathbf{Sb_2S_3} + 2\,(NH_4)_2S_2 = (NH_4)_3SbS_4 + NH_4SbS_3.$$

If the solution of ammonium thioantimonite is boiled for a long time in the air, the red-colored oxysulfide is often precipitated:

$$2\,(NH_4)_3SbS_3 + 4\,O_2 = 2\,(NH_4)_2S_2O_3 + 2\,NH_3\uparrow + H_2O + \mathbf{Sb_2S_2O}.$$

By boiling antimony chloride with sodium thiosulfate, the oxysulfide is also obtained,

$$2\,Sb^{+++} + 3\,S_2O_3^{--} \rightarrow 4\,SO_2\uparrow + \mathbf{Sb_2S_2O},$$

which, on being warmed with ammonium sulfide, redissolves, forming the thio salt.

Antimony trisulfide is also soluble in caustic alkali, forming thio and oxythio salts:

$$\mathbf{Sb_2S_3} + 2\,OH^- = H_2O + OSbS^- + SSbS^-.$$

These thio salts are decomposed by acids, precipitating antimony trisulfide, with evolution of hydrogen sulfide,

$$2\,SbS_3^{---} + 6\,H^+ \rightarrow 3\,H_2S\uparrow + \mathbf{Sb_2S_3};$$
$$2\,SbS_4^{---} + 6\,H^+ \rightarrow 3\,H_2S\uparrow + \mathbf{Sb_2S_5};$$
$$OSbS^- + SSbS^- + 2\,H^+ \rightarrow H_2O + \mathbf{Sb_2S_3}.$$

Boiling a solution of antimony trisulfide in potassium hydroxide or alkali sulfide with bismuth oxide results in the formation of insoluble bismuth sulfide and soluble antimonite

$$\mathbf{Bi_2O_3} + SbS_3^{---} \rightarrow \mathbf{Bi_2S_3} + SbO_3^{---}.$$

If the alkaline thioantimonite solution is boiled with cupric oxide, insoluble cuprous and cupric sulfides and soluble antimonite are formed:

$$4\,\mathbf{CuO} + SbS_3^{---} \rightarrow SbO_4^{---} + \mathbf{Cu_2S} + 2\,\mathbf{CuS}.$$

4. **Zinc** precipitates metallic antimony from solutions of antimony compounds. If a piece of platinum foil and a little zinc are placed in an antimony solution containing hydrochloric acid, so that the two metals touch one another, the antimony is deposited on the platinum in the form of a black stain which does not disappear on removal of the zinc (difference from tin).

Lead, tin and other metals will also cause the same reaction to take place (cf. p. 45). Zinc, however, unlike iron, tin and lead, is likely to carry the reduction farther and stibine gas, SbH_3, is formed with a part of the antimony:

$$2\,Sb^{+++} + 3\,\mathbf{Zn} \rightarrow 3\,Zn^{++} + 2\,\mathbf{Sb}.$$
$$Sb^{+++} + 3\,\mathbf{Zn} + 3\,H^+ \rightarrow 3\,Zn^{++} + SbH_3\uparrow.$$

The stibine behaves like arsine in the Marsh test, but the antimony is less volatile and less soluble in sodium hypochlorite solution.

5. **Potassium Iodide** does not set free iodine when treated with an antimonous solution (difference from antimonic compounds).

6. **Ammonium Thioacetate** and **Sodium Thiosulfate** precipitate antimonous sulfide from acid solutions. Under suitable conditions, "antimony cinnabar" Sb_2S_2O, or a mixture of Sb_2S_3 and some Sb_2O_3, is formed with sodium thiosulfate.

B. Antimonic Compounds

Antimony pentoxide, Sb_2O_5, is formed as a yellow powder by oxidizing antimony with concentrated nitric acid and gently igniting the reaction product (antimonic acid). On strong ignition it loses oxygen and goes over into the very stable antimonous antimonate Sb_2O_4.

The pentoxide dissolves in concentrated hydrochloric acid, forming the pentachloride

$$Sb_2O_5 + 10\ HCl = 5\ H_2O + 2\ SbCl_5.$$

If this solution is treated with water, a white precipitate of antimonic oxychloride, SbO_2Cl, is formed, which, by the addition of more water, is changed on warming into antimonic acid:

$$SbCl_5 + 2\ H_2O \rightleftarrows 4\ HCl + \mathbf{SbO_2Cl},$$
$$\mathbf{SbO_2Cl} + 2\ HOH \rightleftarrows HCl + \mathbf{H_3SbO_4}.$$

Tartaric acid prevents the precipitation of the oxychloride, as with SbOCl (p. 259). Antimony pentoxide is an acid anhydride, and, like the corresponding P_2O_5, can be referred to three acids, orthoantimonic acid, H_3SbO_4; metantimonic acid, $HSbO_3$; and pyroantimonic acid, $H_4Sb_2O_7$, which have all been isolated. The salts of the metantimonic and pyroantimonic acids are the most common. The trimetallic salts of the ortho acid have never been isolated, but the monometallic salts are known to exist. All antimonates, being salts of a weak acid, are very unstable, being easily hydrolyzed by water.

If antimony pentoxide is fused with an excess of caustic potash, the product of the fusion probably contains the trimetallic salt of orthoantimonic acid. If, however, the melt is dissolved in a little water and allowed to crystallize, deliquescent crystals of potassium pyroantimonate, $K_4Sb_2O_7$, are formed.

The ortho salt, which is first formed, is decomposed by water as follows:

$$2\ K_3SbO_4 + H_2O \rightleftarrows 2\ KOH + K_4Sb_2O_7.$$

By the action of considerable cold water (or more quickly by rapid boiling with less water) this deliquescent salt is gradually changed into the acid salt, losing KOH,

$$K_4Sb_2O_7 + 2\ H_2O \rightleftarrows 2\ KOH + K_2H_2Sb_2O_7,$$

which separates out with 6 molecules of water as a granular powder, difficultly soluble in cold water. It dissolves to a considerable extent in water at about 40°–50° C.; this solution is used in testing for sodium, as the sodium salt is very much more insoluble in water.

On boiling the granular potassium salt for a long time with considerable water, it gradually takes on water, forming the easily soluble monometallic salt of orthoantimonic acid,

$$K_2H_2Sb_2O_7 + H_2O \rightleftarrows 2\ KH_2SbO_4,$$

which is obtained, on evaporating the solution, as a gummy mass of the composition $2\ KH_2SbO_4 + H_2O$, but on boiling the aqueous solu-

tion for a long time, more KOH is lost, with the formation of amorphous orthoantimonic acid:

$$KH_2SbO_4 + H_2O \rightleftarrows KOH + \mathbf{H_3SbO_4}.$$

All antimonates are decomposed by acids, amorphous antimonic acid separating out.

The gummy, monometallic salts give an amorphous precipitation with sodium salts, gradually becoming crystalline, while the potassium pyroantimonate gives a crystalline precipitate immediately.

The relations of antimonous to antimonic salts and of antimonites to antimonates, are on the whole, similar to the corresponding relations with arsenic. In the higher state of oxidation the acid properties are more pronounced than the basic properties, but antimony, being lower in same group of the periodic table, is more basic than arsenic.

Reactions of Antimonic Compounds in the Wet Way

1. **Hydrogen Sulfide** precipitates from fairly acid solutions the orange-red pentasulfide:

$$2\,Sb^{+++++} + 5\,H_2S \rightarrow 10\,H^+ + \mathbf{Sb_2S_5}.$$

Antimony pentasulfide is soluble in 12-normal hydrochloric acid, forming antimony *trichloride*, with deposition of sulfur and evolution of hydrogen sulfide:

$$\mathbf{Sb_2S_5} + 6\,HCl \rightarrow 3\,H_2S\uparrow + 2\,S + 2\,SbCl_3.$$

It also dissolves (like the trisulfide) in alkali sulfides, and in alkalies and in ammonia hydroxide, but not in ammonium carbonate. By treatment with an alkali sulfide, a thio salt is obtained,

$$\mathbf{Sb_2S_5} + 3\,S^{--} \rightarrow 2\,SbS_4^{---},$$

which is decomposed by the addition of acids, forming the insoluble pentasulfide with evolution of hydrogen sulfide:

$$2\,SbS_4^{---} + 6\,H^+ \rightarrow 3\,H_2S\uparrow + \mathbf{Sb_2S_5}.$$

Alkalies dissolve the pentasulfide, forming thio and oxy-thio salts:

$$\mathbf{Sb_2S_5} + 6\,OH^- \rightarrow SbS_4^{---} + S \cdot SbO_3^{---} + 3\,H_2O.$$

2. **Hydriodic Acid** reduces antimonic compounds in acid solutions, with separation of iodine (difference from antimonous compounds):

$$Sb^{+++++} + 2\,I^- \rightarrow Sb^{+++} + I_2.$$

3. **Zinc, Tin, Iron, Aluminium, Magnesium** and other metals above hydrogen in the potential series reduce antimony compounds to metallic antimony in acid solutions:

$$\mathbf{5\,Zn} + 2\,SbO_4^{---} + 16\,H^+ \rightarrow \mathbf{2\,Sb} + 5\,Zn^{++} + 8\,H_2O.$$

If an antimony solution is placed in contact with platinum and zinc (both metals touching) the zinc dissolves but the antimony is deposited as a black stain on the platinum.

Zinc, however, unlike tin, iron or lead, reduces some of the antimony to stibine gas, SbH_3.

$$4\ Zn + SbO_4^{---} + 11\ H^+ \rightarrow 4\ Zn^{++} + 4\ H_2O + SbH_3\uparrow.$$

If the stibine is generated in a Marsh apparatus (cf. p. 249), and the gas is conducted through a red-hot glass tube, a mirror of metallic antimony will be deposited, as with arsenic. But as stibine is much more unstable than arsine, and the antimony itself is much less volatile, the mirror is found nearer the heated place than is the case with arsenic — sometimes even before the hottest part of the tube is reached — as the decomposition of the stibine takes place at a much lower temperature than with arsine.

If the stibine is allowed to escape from the tube with the hydrogen, it burns with a pale greenish-white flame to water and antimony trioxide. If a piece of glazed porcelain is held directly over the flame, a deposition of metallic antimony is obtained which is unaffected by a solution of sodium hypochlorite (difference from arsenic).

If stibine is allowed to act upon a solution of silver nitrate, a black precipitate of silver antimonide is formed:

$$SbH_3 + 3\ Ag^+ = \mathbf{Ag_3Sb} + 3\ H^+.$$

Solid silver nitrate is turned yellow at first, then black; exactly the same as by arsine (cf. p. 253).

If a mirror is produced in the Marsh test, antimony may be distinguished from arsenic by the fact that the latter is easily dissolved by sodium hypochlorite solution. Another method for distinguishing between the two metals is as follows:

Detach the tube containing the mirror from the Marsh apparatus and pass hydrogen sulfide through the tube while heating gently in the reverse direction: arsenic is changed to *yellow* sulfide and antimony to orange sulfide. Pass a stream of dry hydrogen chloride through the tube and the orange sulfide will disappear but the arsenic sulfide will remain.

4. **Ammonium Thioacetate** and **Sodium Thiosulfate** behave toward antimony solutions about the same as does hydrogen sulfide.

Reactions of Antimony in the Dry Way

Antimony compounds impart to the flame a pale, greenish-white color. Heated with sodium carbonate on charcoal, a brittle metallic button is obtained, surrounded by a white incrustation.

Compounds containing oxygen are reduced in the upper reducing flame to metal, which is volatile and burns in the upper oxidizing flame to trioxide; the latter can be deposited on a glazed porcelain surface. If the deposit is moistened with silver nitrate solution, and ammonia blown upon it, it becomes black, owing to the separation of metallic silver:

$$\mathbf{Sb_2O_3} + 4\ AgNO_3 + 4\ NH_3 + 2\ H_2O = 4\ NH_4NO_3 + \mathbf{Sb_2O_5} + 4\ \mathbf{Ag}.$$

Antimony sulfide fused with potassium cyanide gives metallic antimony and potassium thiocyanate:

$$3\ KCN + Sb_2S_3 \rightarrow 2\ Sb + 3\ KCNS.$$

If the reaction takes place in a bulb tube, or in a stream of carbon dioxide, a regulus of metal is obtained and not a mirror as with arsenic.

Heating with sodium carbonate and potassium cyanide in a stream of hydrogen gives rise to an antimony mirror not far from the decomposition zone.

TIN, Sn. At. Wt. 118.7

Sp. Gr. = 7.29. M. Pt. = 232° C. B. Pt. = about 1500° C.

Occurrence. — Tin does not occur free in nature, but mostly in the form of the dioxide, as tetragonal tinstone, or cassiterite, isomorphous with rutile (TiO_2), zircon, and polianite (MnO_2).

Tin is a silver-white metal, which is ductile and malleable at ordinary temperatures, but at low temperatures and near the melting-point it is so brittle that it can be powdered. In order to pulverize tin, heat it in a porcelain dish till it melts, remove the flame and quickly crush the substance with a pestle. It soon cools to about 200°, becomes brittle and yields a fine powder.

Below 20°, gray tin is formed and objects made of tin often deteriorate in cold weather owing to the formation of this allotropic modification. When once formed it spreads over the metal. Gray tin is often called, therefore, *tin pest*, and at low temperature the gray tin *infects* the sound metal and makes it powdery.

Above 200° orthorhombic tin crystals are formed which are hard and brittle.

Tin is soluble in hot, concentrated hydrochloric acid with evolution of hydrogen:

$$Sn + 2\ H^+ \rightarrow Sn^{++} + H_2\uparrow.$$

In the presence of platinum the solution takes place more quickly and at a lower temperature. Dilute hydrochloric acid dissolves tin, but very slowly.

Nitric acid, of sp. gr. 1.2 to 1.3, does not dissolve tin, but oxidizes it to metastannic acid:

$$3\ Sn + 4\ HNO_3 + H_2O = 3\ H_2SnO_3 + 4\ NO\uparrow.$$

Cold, dilute nitric acid dissolves the metal very slowly, without any evolution of gas, forming ammonium and stannous nitrates.

In this reaction the tin is given two positive charges and a part of the nitrogen of nitric acid is reduced from a positive valence of five (toward oxygen) to a negative valence of three (toward hydrogen) thereby losing eight charges. Thus one molecule of nitric acid oxidizes four *atoms* of tin and eight more molecules of nitric acid

are required to form stannous nitrate and one to form ammonium nitrate. The whole reaction may be expressed as follows:

$$4\,Sn + 10\,HNO_3 = 4\,Sn(NO_3)_2 + NH_4NO_3 + 3\,H_2O.$$

Aqua regia dissolves tin, forming stannic chloride:

$$3\,Sn + 4\,HNO_3 + 12\,HCl = 4\,NO\uparrow + 8\,H_2O + 3\,SnCl_4.$$

Tin dissolves in dilute sulfuric acid very slowly, but readily in hot concentrated acid, forming stannic sulfate, with evolution of sulfur dioxide:

$$Sn + 4\,H_2SO_4 = 2\,SO_2\uparrow + 4\,H_2O + Sn(SO_4)_2.$$

Tin forms two oxides: stannous oxide, SnO; and stannic oxide, SnO_2. Salts are known corresponding to both these oxides — stannous and stannic salts. The former contain bivalent tin and the latter quadrivalent tin. Tin is more basic in its properties than antimony, but stannous hydroxide is slightly amphoteric (cf. p. 54) and the acid properties of stannic hydroxide are more pronounced.

Stannous Compounds

Stannous oxide (according to the way it is prepared) is either an olive-green or a black powder, which, on being warmed in the air, like all stannous compounds readily changes to stannic oxide. By dissolving stannous oxide (or, better still, the metal itself) in hydrochloric acid, stannous chloride is obtained, which is the most important of all the stannous salts. This salt, with two molecules of water of crystallization, $SnCl_2 + 2\,H_2O$, is the so-called "tin salt" of commerce.

Fresh crystals of "tin salt" will dissolve clear in a little water; if more water is added the solution becomes turbid, owing to the formation of a basic salt,

$$SnCl_2 + H_2O \rightleftarrows HCl + Sn(OH)Cl,$$

which is readily soluble in hydrochloric acid.

The clear concentrated solution also becomes turbid on standing in the air, owing to the formation of the same basic salt.

$$4\,SnCl_2 + O_2 + 2\,H_2O \rightarrow 4\,Sn(OH)Cl + 2\,Cl_2.$$

The chlorine, however, is not set free, but unites with some of the stannous ions, forming stannic ions:

$$Sn^{++} + Cl_2 \rightarrow Sn^{++++} + 2\,Cl^-.$$

If tin tetrachloride is treated with metallic tin, the latter goes into solution and the former is reduced to stannous chloride:

$$SnCl_4 + Sn = 2\,SnCl_2.$$

Consequently, in order to keep a solution of stannous chloride in the stannous condition, hydrochloric acid should be added to prevent the formation of the basic salt, and metallic tin to keep the solution reduced.

Such a solution constantly grows more concentrated, owing to the gradual dissolving of the tin. In order to keep a solution of stannous chloride at a definite concentration (only necessary for purposes of quantitative analysis) the hydrochloric acid solution should be kept out of contact with air in an atmosphere of carbon dioxide without the addition of metallic tin.

Nearly all stannous compounds are colorless; the oxide (as already mentioned) is black and the sulfide dark brown.

Reactions in the Wet Way

1. **Potassium** and **Sodium Hydroxides** produce a white precipitate of gelatinous stannous hydroxide,

$$Sn^{++} + 2\,OH^- \rightarrow Sn(OH)_2,$$

which is readily soluble in an excess of the precipitant, forming alkali stannite:

$$Sn(OH)_2 + OH^- \rightarrow H_2O + HSnO_2^-.$$

The hydroxide is also readily soluble in hydrochloric acid.

The alkaline solution of an alkali stannite is often changed to brownish black or black (particularly on warming, or when very concentrated caustic alkali is used), owing to the separation of either metallic tin or stannous oxide (cf. p. 179):

From dilute potassium hydroxide solutions there gradually separates on standing, or more rapidly on heating, the black monoxide,

$$HSnO_2^- \rightarrow OH^- + SnO;$$

and from quite concentrated alkali the precipitate is almost wholly black metallic tin:

$$2\,HSnO_2^- \rightarrow SnO_3^{--} + H_2O + Sn.$$

2. **Ammonia** and **Alkali Carbonates** precipitate the white hydroxide, which is not absolutely insoluble in an excess of the precipitant:

$$Sn^{++} + 2\,OH^- \rightarrow Sn(OH)_2;$$

$$Sn^{++} + CO_3^{--} + H_2O \rightarrow CO_2\uparrow + Sn(OH)_2.$$

A large quantity of tartaric acid, more than is required in the case of antimony, prevents the precipitation.

3. **Hydrogen Sulfide** produces (in solutions which are not too acid) a brown precipitate of stannous sulfide,

$$Sn^{++} + H_2S \rightarrow 2\,H^+ + \mathbf{SnS},$$

readily soluble in strong hydrochloric acid; therefore no stannous sulfide is precipitated if the solution is very acid. After diluting a strongly acid solution with water, however, stannous sulfide is completely precipitated on saturating the solution with hydrogen sulfide gas.

Stannous sulfide is insoluble in ammonia and ammonium carbonate (difference from arsenic); also in colorless ammonium sulfide (difference from arsenic and antimony); but is readily soluble in yellow ammonium sulfide, forming ammonium thiostannate:

$$\mathbf{SnS} + (NH_4)_2S_2 = (NH_4)_2SnS_3.$$

If the solution of ammonium thiostannate is acidified with any acid, yellow stannic sulfide is precipitated:

$$SnS_3^{--} + 2\,H^+ \rightarrow H_2S\uparrow + \mathbf{SnS_2}.$$

4. **Mercuric Chloride** produces in solutions of stannous salts a white precipitate of mercurous chloride:

$$2\,HgCl_2 + Sn^{++} \rightarrow Sn^{++++} + 2\,Cl^- + \mathbf{Hg_2Cl_2}.$$

But if the stannous chloride is present in excess, the mercurous chloride will be reduced to gray mercury:

$$\mathbf{Hg_2Cl_2} + Sn^{++} \rightarrow Sn^{++++} + 2\,Cl^- + 2\,\mathbf{Hg}.$$

5. The **Gold Test** is much more sensitive. If to a solution of gold chloride a solution containing a trace of stannous chloride is added, finely divided metallic gold will be precipitated,

$$2\,Au^{+++} + 3\,Sn^{++} \rightarrow 3\,Sn^{++++} + 2\,\mathbf{Au},$$

which appears brown by transmitted light, and bluish-green by reflected light.

6. **Metallic Zinc** precipitates tin from both stannous and stannic solutions as a spongy mass, which adheres to the zinc:

$$Sn^{++} + \mathbf{Zn} \rightarrow Zn^{++} + \mathbf{Sn}.$$

The finely-divided, spongy metal is easily soluble in strong hydrochloric acid; the experiment must not, therefore, be made in strongly acid solutions, as the tin is loosened from the zinc by the violent evolution of hydrogen and is redissolved by the acid. The test is best made by adding a drop of the (not too acid) solution to a piece of platinum foil, and then placing a piece of bright zinc so that it comes in contact with both the solution and the platinum. The tin is precipitated partly

on the zinc and partly on the platinum,* in the form of a gray stain, which disappears from the latter as soon as the zinc is removed, provided the solution is still acid (difference from antimony). If the zinc is kept in contact with the acid until the evolution of hydrogen ceases, the tin stain will not disappear from the platinum, because all the acid has been used up. On adding a few drops of concentrated hydrochloric acid to the platinum, the stain quickly disappears with an evolution of hydrogen. The reason why the tin is deposited on the platinum notwithstanding the presence of acid is that a galvanic current is formed by the contact of the zinc with the platinum, which flows from the zinc to the platinum; the platinum thus serves as a cathode, and the tin is deposited upon it. On removing the zinc the current stops and the stain disappears.

7. **Metallic Lead,** as is evident from its position in the electromotive series (cf. pp. 41 and 44), will reduce tin to the metallic state, but the reaction will stop as soon as the concentration of Pb^{++} becomes nearly as large as that of Sn^{++}; when the concentration of Pb^{++} is greater than that of Sn^{++} the reaction will take place in the reverse direction. It requires a relatively low concentration of H^+ to stop both of these reactions, as both tin and lead are higher in the series than hydrogen. In acid solution, however, metallic lead will reduce Sn^{++++} to Sn^{++} (cf. p. 44).

In acid solutions, **metallic antimony** also reduces stannic salts to the stannous condition:

$$2\,\mathbf{Sb} + 3\,Sn^{++++} \rightarrow 2\,Sb^{+++} + 3\,Sn^{++}.$$

8. **Ammonium Thioacetate** precipitates tin completely as sulfide from hot, dilute acid solutions:

$$C_2H_3OS^- + Sn^{++} + H_2O \rightarrow \mathbf{SnS} + HC_2H_3O_2 + H^+.$$

9. **Sodium Thiosulfate** gradually precipitates the tin from solutions which are not too acid. Sometimes the precipitate is chiefly stannous sulfide:

$$Sn^{++} + S_2O_3^{--} + H_2O \rightarrow \mathbf{SnS} + 2\,H^+ + SO_4^{--}.$$

Sometimes the precipitate contains stannic sulfide and metastannic acid:

$$6\,Sn^{++} + 2\,S_2O_3^{--} + 9\,H_2O \rightarrow \mathbf{SnS_2} + 5\,\mathbf{H_2SnO_3} + 2\,\mathbf{S} + 8\,H^+.$$

If the solution is very acid, considerable thiosulfate must be added:

$$S_2O_3^{--} + 2\,H^+ \rightarrow \mathbf{S} + H_2O + SO_2\uparrow,$$

and to some extent the SO_2 reacts with Sn^{++}:

$$3\,Sn^{++} + SO_2 + 6\,H^+ \rightarrow 3\,Sn^{++++} + H_2S\uparrow + 2\,\mathbf{H_2O}.$$

* In weakly acid solutions tin is precipitated chiefly on the zinc; in strongly acid solutions, chiefly on the platinum.

10. **Bismuth Nitrate** added in small quantity to an alkaline solution of a tin salt gives a white precipitate of bismuth hydroxide which rapidly changes to black metallic bismuth.

$$2\ Bi^{+++} + 3\ SnO_2^{--} + 6\ OH^- \rightarrow 3\ SnO_3^{--} + 3\ H_2O + 2\ \mathbf{Bi}.$$

11. **Potassium Ferricyanide** and **Ferric Chloride** added to an acid solution of a stannous salt give a precipitate of Prussian blue:

$$6\ [Fe(CN)_6]^{---} + 8\ Fe^{+++} + 3\ Sn^{++} \rightarrow 3\ Sn^{++++} + 2\ \mathbf{Fe_4[Fe(CN)_6]_3}.$$

The reaction is sensitive but is caused by reducing agents other than stannous chloride. The ferricyanide ion is reduced to ferrocyanide ion which gives a blue color with ferric ions.

12. **Oxalic Acid** precipitates white, granular stannous oxalate from neutral or faintly acid solutions of stannous salts:

$$Sn^{++} + H_2C_2O_4 \rightarrow \mathbf{SnC_2O_4} + 2\ H^+.$$

Ammonium chloride prevents this reaction. A solution of stannous salt containing ammonium chloride and considerable oxalic acid is not acted upon by hydrogen sulfide.

13. **Ammonium Molybdate** in sulfuric acid solution is reduced and gives a blue color with stannous salts. This reaction is sensitive but is caused by other reducing agents also.

14. **Hydrogen Peroxide** added to a solution of stannous salt which has been made as nearly neutral as possible by the addition of alkali hydroxide, gives a white precipitate of stannic hydroxide on heating:

$$Sn^{++} + H_2O_2 + 2\ OH^- \rightarrow \mathbf{Sn(OH)_4}.$$

Stannic Compounds

The stannic compounds (which are all colorless, with the exception of the yellow sulfide, SnS_2) cannot be obtained by the solution of the oxide, SnO_2, from which they are derived, because the oxide is attacked with difficulty by acids. They are obtained indirectly from metallic tin or from stannous compounds.

The simple stannic compounds are all, more or less readily, hydrolyzed by water, so that the analyst almost never meets with them. The nitrate, $Sn(NO_3)_4$, and the sulfate, $Sn(SO_4)_2$, are quickly decomposed in the cold, into acid and stannic hydroxide. The halogen compounds are more stable, and are decomposed only by boiling with considerable water. For the reactions below, therefore, it will be assumed that the tests are made with a solution of stannic chloride.

Stannic chloride is a colorless liquid, which fumes in the air and

boils at 120° C. On adding a little water it solidifies, forming crystals of monoclinic hydrates, $SnCl_4 + 3\ H_2O$, $SnCl_4 + 5\ H_2O$, $SnCl_4 + 8\ H_2O$. The salt with $5\ H_2O$ is used commercially as a mordant in dyeing.

On adding more water to these hydrates they dissolve, forming a clear solution, which on boiling (the freshly-prepared, dilute solution) gradually becomes turbid, owing to the precipitation of voluminous stannic hydroxide:

$$SnCl_4 + 4\ HOH \rightleftarrows 4\ HCl + Sn(OH)_4.$$

If the solution is very dilute it becomes turbid in the cold. The stannic acid thus formed is not precipitated quantitatively, either in the cold or on boiling, because a considerable amount remains in the hydrosole form. By "salting out" the hot solution (best with ammonium nitrate), the stannic acid may be completely precipitated.

A solution of stannic chloride can be most readily obtained for analytical purposes by chlorinating or brominating a solution of stannous chloride.

On adding chlorine to a solution of stannous chloride, stannic chloride is formed in the cold:

$$SnCl_2 + Cl_2 = SnCl_4.$$

As, however, chlorine is colorless in a dilute solution, it is difficult to tell when the oxidation is complete: it is more easily ascertained if bromine is used.

On adding strong bromine water, drop by drop with constant stirring, to a solution of stannous chloride, the bromine color will disappear as long as any stannous chloride remains unchanged, and the solution becomes colored by the bromine only when the oxidation is complete. The solution then contains a mixture of stannic chloride and stannic bromide:

$$2\ SnCl_2 + 2\ Br_2 = SnCl_4 + SnBr_4.$$

Just as platinum tetrachloride combines with hydrochloric acid to form chloroplatinic acid, so tin tetrachloride unites with hydrochloric acid, forming chlorostannic acid, H_2SnCl_6, and yields, like the former, beautifully crystalline, easily soluble salts with the alkalies, of which the ammonium salt $(NH_4)_2[SnCl_6]$ is an article of commerce, being known as "pink salt." The above-mentioned stannic chloride, $SnCl_4$, is sometimes designated as α-stannic chloride, to distinguish it from a compound (to be described later) known as β-stannic chloride (stannyl chloride).

Reactions of the α-Stannic Compounds

1. **Hydrochloric** and **Sulfuric Acids** produce in moderately concentrated solutions of stannic chloride no precipitation, even on long standing (difference from β-stannic compounds). In very dilute sulfuric acid solutions a precipitate of basic sulfate is sometimes obtained. In very dilute hydrochloric acid solutions, also, a slight turbidity is often formed, which increases on boiling the solution:

$$SnCl_4 + 4\ HOH \rightleftarrows 4\ HCl + \mathbf{Sn(OH)_4}.$$

2. **Potassium** and **Sodium Sulfates** produce no precipitation in the cold (difference from stannyl chloride), but on boiling all the tin is precipitated as hydroxide.

3. **Potassium** or **Sodium Hydroxide.** — On adding caustic alkali to a solution of a stannic salt, a voluminous, gelatinous, white precipitate is obtained:

$$SnCl_4 + 4\ OH^- \rightarrow 4\ Cl^- + \mathbf{Sn(OH)_4}.$$

The precipitate has the above formula when dried in the air, and the formula H_2SnO_3 if dried over sulfuric acid.

The precipitate dissolves readily in an excess of alkali hydroxide, forming salts which are not derived from either of the above compounds, but from $H_2[Sn(OH)_6]$, which has itself never been isolated:

$$\mathbf{Sn(OH)_4} + 2\ KOH = K_2[Sn(OH)_6].$$

The hydroxide dissolves in ammonia also, but only in the absence of ammonium salts.

By dissolving in alkali, stannic hydroxide behaves as an acid, and according to Bellucci and Parravano,* the hexahydroxystannic acid stands in the same relation to chlorostannic acid as hexahydroxyplatinic acid to chloroplatinic acid:

$H_2[PtCl_6]$	$H_2[SnCl_6]$
$H_2[Pt(OH)_6]$	$H_2[Sn(OH)_6]$.

The salts of hexahydroxystannic acid are designated briefly as stannates, or α-stannates, to distinguish them from the β-stannates or metastannates, which are derived from the polymer $(H_2SnO_3)_5$ (see p. 273).

The ready solubility of α-stannic acid in cold dilute mineral acids is very characteristic. It dissolves promptly in hydrochloric, nitric, and sulfuric acids, behaving, in this respect, as a base. By boiling the dilute acid solution (particularly the sulfuric acid solution) stannic

* *Z. anorg. Chem.*, **45**, p. 156 (1905).

acid is reprecipitated, which is soluble in cold dilute acids provided the boiling has not been continued too long. In the latter case the β-stannic acid is formed, which is insoluble in dilute acids.

4. **Potassium Carbonate** precipitates stannic acid from stannic chloride solutions; the precipitate dissolves completely in an excess of the reagent (difference from β-stannic acid):

$$SnCl_4 + 2\,K_2CO_3 + 2\,H_2O = 4\,KCl + 2\,CO_2\uparrow + \mathbf{Sn(OH)_4}.$$
$$\mathbf{Sn(OH)_4} + K_2CO_3 \rightarrow K_2SnO_3 + 2\,H_2O + CO_2\uparrow.$$

5. **Sodium Carbonate** behaves similarly, but the precipitate is not so easily dissolved by an excess.

6. **Ammonia** precipitates stannic acid from a solution of stannic chloride; tartaric acid prevents the precipitation (difference from β-stannic acid).

Reactions of the β-Stannic Compounds

(*Metastannates*)

By the oxidation of metallic tin with hot nitric acid of sp. gr. 1.3 stannic nitrate is first formed, which, by boiling with water, is completely hydrolyzed, forming nitric acid and metastannic acid.

Metastannic acid is a white powder insoluble in nitric acid, and when dried over sulfuric acid has the formula H_2SnO_3. This is of the same empirical composition as the hydroxide precipitated by treating a stannic chloride solution with alkalies, though differing essentially from it in many reactions.

Although the α-stannic acid (as already mentioned) is easily soluble in dilute mineral acids, the β-stannic acid is practically insoluble therein.

1. If the β-stannic acid is treated for a short time with concentrated hydrochloric acid, a chloride is formed which is insoluble in hydrochloric acid, but readily soluble in water. The solution contains the so-called β-stannic chloride (though the designation stannyl chloride would be more suitable) of the composition, $Sn_5O_5Cl_2(OH)_8$.*

2. On treating the aqueous solution of stannyl chloride with hydrochloric acid, almost all the tin is reprecipitated in the form of a highly chlorinated compound of the composition $Sn_5O_5Cl_4(OH)_6 + 4\,H_2O$.†

3. If an aqueous solution of stannyl chloride is heated to boiling, almost all the tin is precipitated as β-stannic acid, which is insoluble in dilute acids.

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* R. Engel, *Chem. Ztg.*, **1897**, pp. 309 and 859.

† Weber, *Jahresber.*, **1869**, 244. and *Pogg. Ann.*, **122**, 358.

This differing behavior of the two acids, as well as of the two chlorides, can be explained as follows: Silicic acid, which is closely related to stannic acid, exists in innumerable silicates in different polymeric forms. Thus, with the minerals of the pyroxene and amphibole groups, wollastonite, $CaSiO_3$, is a derivative of ordinary metasilicic acid and tremolite, $CaMg_3Si_4O_{12}$, is a derivative of $(H_2SiO_3)_4$.* It is highly probable that the stannic acid can exist in analogous polymers. One of these polymers apparently corresponds to the composition $(H_2SnO_3)_5$.

If such a compound is treated with hydrochloric acid, the hydroxyl groups will, first, be replaced by chlorine, and a compound will be obtained containing tin, oxygen, and chlorine, e.g., $Sn_5O_5Cl_{10}$.

This hypothetical compound of the β-stannic acid is hydrolyzed, forming different chlorides of varying solubilities. Thus R. Engel found that the chloride $Sn_5O_5Cl_2(OH)_8$ is soluble in water; and Weber showed that from an aqueous solution of the latter, hydrochloric acid precipitates the compound $Sn_5O_5Cl_4(OH)_6 + 4\ H_2O$.

The reaction which takes place on dissolving the β-stannic acid in hydrochloric acid and water may be expressed satisfactorily by the following equations:

$$\underset{\substack{\beta\text{-stannic acid}\\ \text{or}\\ \text{Metastannic acid}}}{\mathbf{Sn_5O_5(OH)_{10}}} + 10\ HCl = 10\ H_2O + \mathbf{Sn_5O_5Cl_{10}}\ \text{(insoluble in HCl)};$$

$$\mathbf{Sn_5O_5Cl_{10}} + 8\ H_2O \rightleftarrows 8\ HCl + Sn_5O_5Cl_2(OH)_8\ \text{(soluble in water)};$$

$$Sn_5O_5Cl_2(OH)_8 + 2\ HCl \rightleftarrows 2\ H_2O + \mathbf{Sn_5O_5Cl_4(OH)_6}\ \text{(insoluble in HCl)}.$$

On boiling the aqueous solution, complete hydrolysis takes place:

$$Sn_5O_5Cl_2(OH)_8 + 2\ HOH = 2\ HCl + \mathbf{Sn_5O_5(OH)_{10}}.$$

If the β-stannic acid is treated for a long time with concentrated hydrochloric acid, the Sn_5O_5 group is finally broken down, and the tin goes into solution in the form of ordinary α-stannic chloride:

$$\mathbf{Sn_5O_5(OH)_{10}} + 20\ HCl = 15\ H_2O + 5\ SnCl_4.$$

Other reactions of stannyl chloride (β-stannic chloride) are:

4. **Sulfuric Acid** precipitates from solutions of stannyl chloride white stannyl sulfate, which on being washed with water is completely changed to β-stannic acid (difference from α-stannic chloride).

5. **Potassium** and **Sodium Sulfates** cause the same reaction as sulfuric acid.

6. **Potassium Hydroxide** throws down in solutions of stannyl chloride a voluminous precipitate of β-stannic acid, which does not

* GROTH, *Tabellarische Uebersicht d. Min.*, **1898**, p. 148.

dissolve in an excess of the concentrated precipitant, but forms a β-stannate easily soluble in dilute caustic potash solution:

$$(a)\ Sn_5O_5Cl_2(OH)_8 + 2\,KOH = 2\,KCl + \underset{\beta\text{-stannic acid}}{Sn_5O_5(OH)_{10}};$$

$$(b)\ Sn_5O_5(OH)_{10} + 2\,KOH = 2\,H_2O + \underset{\text{potassium } \beta\text{-stannate}}{Sn_5O_5(OK)_2(OH)_8}.$$

By long treatment of the potassium β-stannate with concentrated caustic potash, it gradually goes into solution, forming potassium α-stannate. This change takes place more readily by fusing β-stannic acid with solid potassium hydroxide in a silver crucible.

If a dilute solution of a mineral acid is added to the β-potassium stannate, a voluminous precipitate is formed, consisting partly of β-stannic acid (insoluble in an excess of mineral acids) and partly of α-stannic acid (readily soluble in an excess of the acid). The latter compound is formed when a very concentrated solution of caustic potash was used in forming the potassium salt.

7. **Ammonia** also precipitates β-stannic acid, even in the presence of tartaric acid (difference from α-stannic chloride).

As we have seen, the α-compounds may be readily changed into β-compounds and conversely. *The dilute aqueous solutions of the α-compounds are gradually changed, at the ordinary temperature, into β-compounds, but more quickly on boiling;* thus stannic chloride changes to stannyl chloride:

$$5\,SnCl_4 + 13\,H_2O = 18\,HCl + Sn_5O_5Cl_2(OH)_8.$$

The β-compounds are changed into α-compounds by boiling with concentrated hydrochloric acid or with concentrated caustic potash.

8. **Hydrogen Sulfide** precipitates (from not too acid solutions) yellow stannic sulfide from both the α- and the β-compounds:

$$SnCl_4 + 2\,H_2S \rightleftarrows 4\,HCl + SnS_2;$$

$$Sn_5O_5Cl_2(OH)_8 + 10\,H_2S \rightleftarrows 2\,HCl + 13\,H_2O + 5\,SnS_2.$$

From β-stannic solutions hydrogen sulfide produces a precipitate, but very slowly, the SnS_2 remaining largely in the hydrosole form. By the addition of salts it is coagulated, and separates out in a flocculent form, usually mixed with β-stannic acid. If the stannyl chloride solution is heated on the water-bath in a pressure flask, the tin is quickly precipitated as greenish-yellow sulfide.

Stannic sulfide is soluble in hydrochloric acid; hydrogen sulfide will cause no precipitation, therefore, if the solution is very acid. If such a solution, saturated with hydrogen sulfide, is greatly diluted, the sulfide will precipitate out.

The yellow sulfide is the thio-anhydride of the thio-acid; it dissolves, therefore, in alkali sulfide, forming salts soluble in water:

$$\mathbf{SnS_2} + (NH_4)_2S \rightarrow (NH_4)_2\mathbf{SnS_3}.$$

Acids precipitate from such a solution the yellow stannic sulfide

$$SnS_3^{--} + 2\,H^+ \rightarrow H_2S\uparrow + \mathbf{SnS_2}.$$

The sulphide is slightly soluble in ammonia but scarcely at all in ammonium carbonate (difference from arsenic). By means of concentrated nitric acid it is easily oxidized to β-stannic acid; or by roasting in the air it can be completely changed to tin dioxide.

The sulfide obtained in the dry way, known as "mosaic gold," is not attacked by nitric acid, and is also insoluble in alkali sulfides. It dissolves on treatment with aqua regia, forming stannic chloride with separation of sulfur. Like native tinstone, it is most readily brought into solution by fusing with sodium carbonate and sulfur (see below).

Although stannic sulfide is yellow when pure, it often appears brown when precipitated with other metallic sulfides by hydrogen sulfide.

Tin has a distinct tendency to form complex ions from which hydrogen sulfide does not give the sulfide precipitate. Thus oxalic acid prevents the precipitation of tin (35 to 40 parts of oxalic acid to 1 of tin). Similarly, hydrofluoric acid and phosphoric acid prevent the formation of stannic sulfide.

9. **Ammonium Thioacetate** precipitates stannic sulfide from hot, acid solutions:

$$2\,C_2H_3OS^- + Sn^{++++} + 2\,H_2O \rightarrow \mathbf{SnS_2} + 2\,HC_2H_3O_2 + 2\,H^+.$$

Sodium Thiosulfate precipitates a mixture of stannic hydroxide, stannic sulfide and sulfur when added to an acid solution of stannic salt:

$$Sn^{++++} + 2\,S_2O_3^{--} + 2\,H_2O \rightarrow \mathbf{SnS_2} + 4\,H^+ + 2\,SO_4^{--}.$$

$$Sn^{++++} + 2\,S_2O_3^{--} + H_2O \rightarrow \mathbf{H_2SnO_3} + 2\,\mathbf{S} + 2\,SO_2\uparrow.$$

10. **Metallic Zinc** precipitates spongy, metallic tin:

$$2\,\mathbf{Zn} + Sn^{++++} \rightarrow \mathbf{Sn} + 2\,Zn^{++}.$$

If the zinc is in contact with platinum, the tin does not deposit upon the platinum, as does antimony, but upon the zinc.

11. **Metallic Iron** reduces stannic chloride to stannous chloride but not to the metallic condition:

$$Sn^{++++} + \mathbf{Fe} \rightarrow Fe^{++} + Sn^{++}.$$

This reaction takes place even in the cold. It also takes place on boiling with copper or with antimony:

$$Cu + Sn^{++++} \rightarrow Sn^{++} + Cu^{++}.$$

$$2\,Sb + 3\,Sn^{++++} \rightarrow 3\,Sn^{++} + 2\,Sb^{+++}.$$

12. **Mercuric Chloride** produces no precipitation in solutions of stannic salts.

Tin dioxide as it occurs in nature, and the artificially produced oxide after strong ignition, are both insoluble in all acids. They can be brought into solution by the following methods:

1. Fusion with sodium carbonate and sulfur;
2. Fusion with caustic potash or soda;
3. Fusion with potassium cyanide;
4. Reduction by hydrogen at a high heat.

(1) *Fusion with Sodium Carbonate and Sulfur.* — Place the dry substance in a small porcelain crucible, mix with six times as much anhydrous sodium carbonate and sulfur (equal parts mixed together), cover the crucible, and heat over a small flame until the excess of sulfur has distilled off and burned. This operation requires about twenty minutes. Allow the crucible to cool and then treat its contents with hot water, and filter if necessary:

$$2\,SnO_2 + 2\,Na_2CO_3 + 9\,S = 3\,SO_2 + 2\,Na_2SnS_3 + 2\,CO_2.$$

If iron, lead, copper, or any other metal that forms a sulfide insoluble in water and ammonium polysulfide is present, it remains undissolved as sulfide, and is separated from the tin by filtration.

(2) *Fusion with Sodium Hydroxide.* — Melt the sodium hydroxide in a silver crucible, placed within a porcelain crucible to protect the silver from the injurious action of the gas flame. When the fusion has become quiet, owing to the expulsion of all the excess water, cool somewhat and add the finely-powdered, dry tin dioxide. Heat until the fusion is clear. After cooling dissolve the melt in water:

$$SnO_2 + 2\,NaOH = Na_2SnO_3 + H_2O.$$

Stannic oxide is not completely attacked by fusion with sodium or potassium carbonate.

(3) *Fusion with Potassium Cyanide.* — Melt some potassium cyanide in a porcelain crucible, add the powdered stannic oxide and fuse the mixture until the separated tin has melted together:

$$SnO_2 + 2\,KCN = 2\,KCNO + Sn.$$

After cooling, extract the mass with water, filter off the tin, flatten it into foil and dissolve it in concentrated hydrochloric acid.

(4) *Reduction in a Stream of Hydrogen.* — Place the substance in a platinum boat and insert the latter in a glass tube, open at both ends, which is made of difficultly fusible glass. Pass hydrogen through the tube in the cold until the air has been driven out, and then heat to dull redness until no more water is formed:

$$SnO_2 + 2\,H_2 = 2\,H_2O + Sn.$$

Finally cool and dissolve the metal in hydrochloric acid.

Reactions in the Dry Way

If a tin salt is heated with soda (or potassium cyanide) on charcoal, usually only a small malleable button is obtained, which, on taking away the flame, is immediately covered with a white coating of oxide. This can be observed when the flame is allowed to play upon the fusion. If the product is crushed in an agate mortar, a small flake of metallic tin is obtained, which can be distinguished from silver and lead by its insolubility in nitric acid, and by its solubility in hydrochloric acid. This reaction is particularly suitable for the charcoal-stick test. The borax bead which has been colored pale blue by copper becomes a transparent ruby red in the reducing flame if a trace of tin is added. This is a very sensitive reaction.

By heating stannous or stannic sulfide in chlorine, or by igniting it with a mixture of 5 parts ammonium chloride and 1 part ammonium nitrate, complete volatilization of the tin as stannic chloride takes place. By using a stream of carbon dioxide which has passed through bromine, stannic bromide is formed and distills off.

All tin compounds are reduced to metallic tin by heating with potassium cyanide.

GOLD, Au. At. Wt. 197.2

Sp. Gr. = 19.33. M. Pt. = 1063° C.

Occurrence. — Gold usually occurs native in quartz and in river sands; also as telluride of gold in sylvanite, $(AuAg)_2Te_3$, and in nagyagite, $(PbAu)_2(TeSSb)_3$, and is found in small amounts in many pyrite and other sulfide ores.

Metallic gold is of a yellow color and melts without being oxidized. It is the most ductile of all metals, and may be hammered into exceedingly thin leaves, which are transparent, with a bluish-green color.

Commercial gold is usually alloyed with copper, silver, or with both metals. Pure gold is designated as 24-carat gold or $^{1000}/_{1000}$ fine. Fourteen-carat gold contains 14 parts of gold to 10 parts of other metal and 18-carat gold contains 18 parts of gold and 6 parts of alloy; the former, therefore, contains 58.3 per cent and the latter 75 per cent of pure gold.

The proper solvent for gold is aqua regia, but it is also soluble in bromine and chlorine water, forming a trihalogen compound:

$$2\,Au + 2\,HNO_3 + 6\,HCl = 4\,H_2O + 2\,NO\uparrow + 2\,AuCl_3,$$

$$2\,Au + 3\,Br_2 = 2\,AuBr_3.$$

Gold is not attacked by mineral acids. It is dissolved by potassium cyanide solution in contact with the oxygen of air. It forms two oxides: aurous oxide, Au_2O; and auric oxide, Au_2O_3.

Both of these are exceedingly unstable; on gentle ignition they lose oxygen and are changed to metal (a property common to all "noble" metals).

All gold salts are unstable; even the most stable salt of all, the chloride, $AuCl_3$, is changed by gentle ignition into yellowish-white aurous chloride, AuCl:

$$AuCl_3 = AuCl + Cl_2 \uparrow .$$

On stronger ignition the third atom of chlorine is lost, and the yellow metal itself is left behind.

Aurous chloride, AuCl, is insoluble in water, but on being boiled with water for some time, or more slowly in the cold, it is changed to auric chloride with deposition of metal:

$$3\,AuCl = AuCl_3 + 2\,Au.$$

The solution obtained by dissolving gold in aqua regia always contains auric chloride, so that only the reactions of auric compounds are of interest to the analytical chemist. Auric chloride unites with hydrochloric acid, forming chlorauric acid,

$$AuCl_3 + HCl = H[AuCl_4],$$

which yields beautifully crystalline salts.

Gold chloride is soluble in ether and can be extracted from its aqueous solutions by means of this solvent.

Auric salts are mostly yellow and readily soluble in water. The sulfide is black and soluble only in aqua regia.

Reactions in the Wet Way

A solution of chlorauric acid, $H[AuCl_4]$, should be used for these reactions.

1. **Potassium** or **Sodium Hydroxide.** — If caustic alkali is cautiously added to a concentrated gold solution, a reddish-brown, voluminous precipitate of auric hydroxide is obtained, which looks exactly like ferric hydroxide. If more caustic alkali is added, however, the gold hydroxide redissolves, forming alkali aurate:

$$Au^{+++} + 3\,OH^- \rightarrow Au(OH)_3;\ Au(OH)_3 + OH^- \rightarrow 2\,H_2O + [AuO_2]^-.$$

If the bright-yellow solution of potassium aurate is carefully acidified with nitric acid, a precipitate of reddish-brown auric acid is thrown down, which is soluble in nitric acid, but is reprecipitated, for the most part, by diluting and boiling.

As a rule, potassium hydroxide yields no precipitate in solutions

of gold chloride, because the gold solution is usually so dilute that the amount of alkali added is sufficient to form the aurate at once.

2. **Ammonia** throws down a yellowish mixture of gold iminochloride, Au(NH)Cl, and gold iminoamide, $Au(NH)NH_2$,

$$AuCl_3 + 3\,NH_3 \rightarrow 2\,NH_4Cl + \mathbf{Au(NH)Cl},$$

$$AuCl_3 + 5\,NH_3 \rightarrow 3\,NH_4Cl + \mathbf{Au(NH)NH_2},$$

which explodes in a dry condition on warming or by concussion (fulminating gold.*)

The most important reactions for the detection of gold are those which depend upon the extreme readiness with which the auric compounds are reduced. Auric compounds are strong oxidizing agents.

3. **Ferrous Salts** precipitate at ordinary temperatures from neutral or acid solutions all the gold as a brown powder (difference from platinum):

$$Au^{+++} + 3\,Fe^{++} \rightarrow 3\,Fe^{+++} + \mathbf{Au}.$$

4. **Oxalic Acid** precipitates all of the gold in the cold, but more quickly on warming (difference from platinum):

$$2\,Au^{+++} + 3\,H_2C_2O_4 \rightarrow 6\,H^+ + 6\,CO_2\uparrow + 2\,\mathbf{Au}.$$

The presence of considerable acid prevents this reaction.

5. **Arsine** and **Stibine** precipitate gold completely:

$$2\,Au^{+++} + AsH_3 + 3\,H_2O \rightarrow H_3AsO_3 + 6\,H^+ + 2\,\mathbf{Au}.$$

6. **Sulfurous Acid** reduces gold solutions:

$$2Au^{+++} + 3\,SO_2 + 6\,H_2O \rightarrow 12\,H^+ + 3\,SO_4^{--} + 2\,\mathbf{Au}.$$

7. **Stannous Chloride** causes the following reaction to take place:†

$$2\,Au^{+++} + 3\,Sn^{++} \rightarrow 3\,Sn^{++++} + 2\,\mathbf{Au}.$$

If the solution tested is strongly acid with hydrochloric acid, the precipitate is pure gold and has the characteristic dark-brown color of the finely divided metal. In very dilute weakly acid solutions the so-called purple of Cassius is thrown down, which consists of colloidal gold and tin hydroxide.‡

Purple of Cassius is soluble in ammonia and in dilute caustic potash solution, forming reddish liquids. These solutions when cold remain clear for a long time and can even be boiled without decomposition. As the solution is concentrated a flocculent precipitate is formed which will dissolve on the addition of more ammonia.

The brown coloration can be distinctly seen if 0.3 mg. gold is dissolved in 100 cc. of the solution; if less than 0.3 mg. of gold is present, only a yellowish coloration is obtained.

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* Raschig, *Ann. Chem. Pharm.*, **235** (1886), 325.

† Theodor Döring, *Chem. Centralbl.*, **1900**, I, p. 735.

‡ Zsigmondy, *Ann. Chem. Pharm.*, **301** (1898), 361.

8. **Hydrogen Peroxide** * in alkaline solution immediately precipitates the gold as finely divided metal:

$$2\,Au^{+++} + 3\,H_2O_2 + 6\,OH^- \rightarrow 6\,H_2O + 3\,O_2\uparrow + 2\,Au.$$

The precipitated metal appears brownish-black by reflected light, but bluish-green by transmitted light; 0.03 mg. gold in 10 cc. of liquid suffices to give a reddish coloration with a bluish shimmer.

9. **Zinc.** — The following gold test is very sensitive: † To a few drops of a dilute gold solution add a few drops of arsenic acid, two or three drops of ferric chloride solution, and two to three drops of hydrochloric acid. Dilute the mixture to 100 cc., and drop in a piece of zinc. Around the zinc the solution assumes a purple color, which, by moving the zinc in the solution, is disseminated through it, making it appear pink or purple.

If the solution contains 0.03 mg. of gold, within fifteen minutes a beautiful reddish color will be noticed.

Besides the above reagents many others, such as formaldehyde in the presence of alkali, hydrazine sulfate, etc., are capable of reducing gold from its solutions.

10. **Hydrogen Sulfide** precipitates, in the cold, black gold disulfide from gold solutions:

$$2\,Au^{+++} + 3\,H_2S \rightarrow 6\,H^+ + S + Au_2S_2.$$

Gold disulfide is insoluble in acids; but is readily soluble in aqua regia, forming auric chloride, $AuCl_3$.

The disulfide is difficultly soluble in ammonium sulfide, but more readily soluble in potassium polysulfide, forming a sulfo salt:

$$Au_2S_2 + K_2S_2 = 2\,KAuS_2.$$

From this solution hydrochloric acid precipitates a yellowish-brown sulfide:

$$2\,KAuS_2 + 2\,H^+ \rightarrow 2\,K^+ + H_2S + Au_2S_3(?).$$

From a hot solution, hydrogen sulfide precipitates brown, metallic gold:

$$8\,Au^{+++} + 3\,H_2S + 12\,H_2O \rightarrow 30\,H^+ + 3\,SO_4^{--} + 8\,Au.$$

The finely divided metallic gold is soluble in hot potassium or sodium polysulfide, forming a thio salt:

$$2\,Au + K_2S_4 \rightarrow 2\,KAuS_2.$$

On account of its softness, gold is always alloyed with silver and copper when used for coins or for jewelry. If such an alloy is treated with nitric acid, the copper and silver are dissolved and the gold usually remains as a brownish powder. To

* Vanino and Seemann, *Ber.*, **1899**, 1968.

† *Pharm. Chem. Centralbl.*, **27**, 321.

prove the presence of gold, filter through a small filter, dry the filter, roll up the paper and wrap a platinum wire around it. Set fire to the paper and allow it to burn quietly. The ash must not be too strongly heated, for the gold would then melt and alloy with the platinum wire. Melt the ash with a little sodium carbonate on a charcoal stick; a gold button forms with the characteristic yellow color. The gold button can be pressed into a leaf in the agate mortar, transferred to a watch-glass, and dissolved in a little aqua regia, forming auric chloride. Carefully evaporate the solution to dryness, dissolve the residue in a little water, add a dilute solution of stannous chloride, and the presence of gold is shown by the formation of the purple of Cassius. The hydrogen peroxide and zinc tests are still more delicate (see p. 281).

If it is a question of detecting very small amounts of gold (as in the case of many copper coins), the above method is unsuitable. In such cases, extract the gold and silver by scorification and cupellation. Melt 5 to 10 gms. of the auriferous copper (or more in some cases) with 120 gms. of pure lead in a flat dish of infusible stone (a scorifying-dish), in a muffle with access of air. The copper and a part of the lead are oxidized, and the oxide unites with the silica of the dish to form a readily fusible slag, which eventually covers the unaffected lead and the dissolved silver and gold. This operation is known as *scorification*. When this point is reached, pour the molten mass into an iron scorification pan, previously well chalked. As soon as the mass becomes cool, remove it from the pan, and hammer the slag from the enclosed lead button and weigh the latter. Then put it on a *cupel* (a sort of crucible made of bone ash), of about the same weight as the lead button or a little heavier. Place the cupel in the muffle and again heat with ready access of air. The lead melts and is oxidized; the resulting lead oxide melts at 980° C. and is partly absorbed by the porous cupel and partly volatilized, leaving a kernel of silver and gold behind. Flatten the metallic kernel to foil and treat it with 6-normal nitric acid, which dissolves the silver, leaving the gold, usually in the form of powder. Filter off the gold, dry, and melt it, as above described, upon the charcoal stick. If the alloy of gold and silver (obtained after cupellation) contains three parts of silver to one part of gold, the gold remains after separation with nitric acid as a thin, coherent, brownish mass which becomes hard on igniting, with the characteristic gold color. If the proportion of silver to gold is greater than 3 : 1, the separation by means of nitric acid will be complete and the gold will be left as a powder. If the ratio of silver to gold is less than 3 : 1, the separation by means of nitric acid is incomplete, and the gold residue usually appears yellow, and still contains some silver. In this case, add more silver with 1 gm. of lead and subject the mixture once more to cupellation, when the subsequent separation by means of nitric acid will be complete.

In order to detect very small amounts of gold in ores, a similar procedure is used.

If a muffle furnace is not available, the more tedious wet process must be used. For example, if it is desired to detect the presence of gold in pyrites, roast a large amount of the ore in the air until all the sulfur has been burned off, then treat with bromine water, and allow to stand twelve hours. Filter the solution (which now contains all of the gold as auric bromide) and boil off the excess of bromine. Add ferrous sulfate and a little sulfuric acid, boil the solution again and filter through a small filter. Wash the residue on the filter, dry and then melt it on the charcoal stick.

According to these methods a fractional part of a milligram of gold can be detected with certainty

Reactions in the Dry Way

All compounds of gold, when heated with soda on the charcoal stick, yield a malleable, metallic button, soluble only in aqua regia. The solution in the latter reagent should be evaporated, the residue dissolved in water and tested with stannous chloride, hydrogen peroxide, or zinc.

PLATINUM, Pt. At. Wt. 195.2

Sp. Gr. = 21.48. M. Pt. = 1755° C.

Occurrence. — Platinum is found free in nature, usually accompanied by the other so-called platinum metals.

Metallic platinum is grayish white; in a finely-divided state it is grayish black. The metal is not ordinarily attacked by mineral acids;* it dissolves in aqua regia, forming chloroplatinic acid, $H_2[PtCl_6]$ (not platinum chloride, $PtCl_4$). If, however, the platinum is alloyed with sufficient silver, it dissolves in nitric acid, forming a yellow solution. Like tin, platinum forms two oxides: platinum monoxide, PtO; and platinum dioxide, PtO_2.

Both oxides may be obtained by the careful ignition of the corresponding hydroxides. They are exceedingly unstable, being decomposed by gentle ignition into metal and oxygen; all the remaining platinum compounds behave similarly.

The most important of the platinum compounds are the chlorides. By dissolving platinum in aqua regia, chloroplatinic acid is always obtained, from which the di- and tetrachlorides may be derived; these unite with hydrochloric acid to form the complex acids

$PtCl_4 + 2\ HCl = H_2[PtCl_6]$ (Chloroplatinic acid — orange red crystals),

$PtCl_2 + 2\ HCl = H_2[PtCl_4]$ (Chloroplatinous acid — known only in solution).

The aqueous solution of chloroplatinic acid is yellowish orange; a solution of chloroplatinous acid, containing the same quantity of platinum, is dark brown.

The potassium and ammonium salts of chloroplatinous acid are soluble in water; the corresponding salts of chloroplatinic acid are difficultly soluble in water and insoluble in 75 per cent alcohol.

* By boiling concentrated sulfuric acid in platinum dishes 10 cc. of acid will dissolve 3.8 mg. of platinum in ten minutes. Le Roy and McCay, 8th *Internatl. Cong. App. Chem.*, **1**, 351 (1912).

prove the presence of gold, filter through a small filter, dry the filter, roll up the paper and wrap a platinum wire around it. Set fire to the paper and allow it to burn quietly. The ash must not be too strongly heated, for the gold would then melt and alloy with the platinum wire. Melt the ash with a little sodium carbonate on a charcoal stick; a gold button forms with the characteristic yellow color. The gold button can be pressed into a leaf in the agate mortar, transferred to a watch-glass, and dissolved in a little aqua regia, forming auric chloride. Carefully evaporate the solution to dryness, dissolve the residue in a little water, add a dilute solution of stannous chloride, and the presence of gold is shown by the formation of the purple of Cassius. The hydrogen peroxide and zinc tests are still more delicate (see p. 281).

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According to these methods a fractional part of a milligram of gold can be detected with certainty

9. **Carbon Monoxide,** on being passed into a solution of chloroplatinic acid containing sodium acetate, colors the solution a beautiful red owing to the formation of colloidal platinum (difference from palladium). After standing some time all the platinum is precipitated as a black powder and the supernatant liquid is colorless:

$$H_2[PtCl_6] + 2\,CO + 6\,C_2H_3O_2^- + 2\,H_2O \rightarrow 6\,Cl^- + 6\,HC_2H_3O_2 + 2\,CO_2\uparrow + \mathbf{Pt.}$$

10. **Zinc,** cadmium, magnesium or aluminium reduces chloroplatinic acid to metal:

$$H_2[PtCl_6] + 3\,\mathbf{Zn} \rightarrow 3\,ZnCl_2 + H_2\uparrow + \mathbf{Pt.}$$

The precipitated metal is in such a finely divided condition that it tends to run through the filter, especially on being washed with pure water; by washing with salt solution a clear filtrate can be obtained.

11. **Hydrazine Hydrochloride,** $N_2H_4{\cdot}2\,HCl$, readily reduces chloroplatinic acid in ammoniacal solutions; some of the platinum is deposited as a mirror upon the sides of the vessel containing the solution.

$$(NH_4)_2[PtCl_6] + N_2H_4{\cdot}2\,HCl + 6\,NH_3 \rightarrow 8\,NH_4Cl + N_2\uparrow + \mathbf{Pt.}$$

12. **Formaldehyde** in alkaline solutions precipitates the platinum as extremely-finely-divided *platinum black:*

$$H_2[PtCl_6] + HCHO + 6\,OH^- \rightarrow CO_2\uparrow + 6\,Cl^- + 5\,H_2O + \mathbf{Pt.}$$

The precipitate may be washed with alkali salt solutions, but with pure water a black colloidal solution of platinum is formed.

Preparation of Chloroplatinic Acid for Use as a Reagent

Since chloroplatinic acid is used not only for the qualitative detection but also for the quantitative determination, of ammonium and potassium methods for preparing a solution of this reagent will be described.

1. *Preparation of Chloroplatinic Acid from Metallic Platinum.* — Commercial platinum usually contains iridium; and although pure iridium is practically insoluble in aqua regia, it dissolves considerably in this reagent if it is alloyed with platinum. Moreover, platinum forms with aqua regia not only chloroplatinic acid, but also chloroplatinous acid (the most harmful of all impurities for this reagent) and nitroso-platinic chloride, $[PtCl_6](NO)_2$. These facts must be borne in mind in preparing the reagent.

First of all, clean the strips of platinum by boiling them with concentrated hydrochloric acid and washing with water. Then place the platinum in a capacious flask, pour over it concentrated hydrochloric acid, and add nitric acid little by little, with continuous, gentle heating on the water-bath. All the platinum and some iridium are thus brought into solution, while some of the latter metal usually remains undissolved as a black powder.

Decant the solution (without stopping to filter) into a porcelain evaporating-dish and evaporate to sirupy consistency. Dissolve the residue in water, add some sodium formate and sodium carbonate until the solution is slightly alkaline. Heat

the solution to boiling, which causes the precipitation of the platinum and iridium in a few minutes as a black powder. This operation should be performed in a large evaporating-dish, on account of the violent effervescence due to the escape of carbon dioxide. Pour off the supernatant liquid and wash the residue several times with hydrochloric acid to remove the sodium salt, and finally with water to remove the acid. Dry the powder, which contains iridium and platinum (in the presence of one another, but not alloyed together) and ignite it strongly in a porcelain crucible over the blast-lamp (whereby the iridium is made insoluble in aqua regia), and then weigh. Dissolve the ignited gray metal (at as low a temperature as possible) in hydrochloric acid, with gradual addition of nitric acid. Considerable quantities of nitroso-platinic chloride are formed by this operation. On evaporating with water, this compound is decomposed into chloroplatinic acid, with evolution of oxides of nitrogen:

$$[PtCl_6](NO)_2 + H_2O = NO_2\uparrow + NO\uparrow + H_2[PtCl_6].$$

As, however, a part of the NO_2 (or N_2O_4) remains in solution, some more nitric and nitrous acids are formed by the action of water,

$$N_2O_4 + H_2O = HNO_3 + HNO_2,$$

which yield nitrosyl chloride with the hydrochloric acid present, and cause the formation of more nitroso-platinic chloride.

It is necessary, therefore, to evaporate the solution alternately with hydrochloric acid and with water until no more nitrous fumes are given off. The solution thus obtained always contains some chloroplatinous acid, and is intensely brown. In order to change this last compound into chloroplatinic acid, saturate the warm solution with chlorine gas (whereby its color becomes much lighter) and then evaporate (at as low temperature as possible) till it becomes of sirupy consistency. After cooling, the sirup crystallizes to a yellowish-brown mass, which may be dissolved in a little cold water, and the insoluble iridium filtered off.

If there is a considerable amount of the latter metal, ignite it in a porcelain crucible and weigh. The weight of the iridium should be deducted from the previous weight of the mixture, in order to find out how much platinum remains in solution.

Dilute the filtered solution with water until 100 cc. of the solution contain 10 gms. of platinum.

2. *Preparation of Chloroplatinic Acid from Platinum Residues.* — These residues consist of potassium chloroplatinate and the alcoholic wash-waters.

By evaporating an alcoholic solution of chloroplatinic acid, chloroplatinous acid and ethylene are formed, which yield ethylene platinous chloride; this last compound gives no precipitation with potassium or ammonium salts:

$$\underset{}{H_2[PtCl_6]} + 2\underset{\text{Alcohol}}{C_2H_5OH} = \underset{\text{Aldehyde}}{CH_3CHO} + 4\,HCl + \underset{}{C_2H_4[PtCl_2]} + H_2O$$

On evaporating an alcoholic solution of this soluble organic platinum compound, it is changed into an insoluble powder which is explosive when dry, insoluble in acids, and completely decomposed by strong ignition only.

To separate platinum, therefore, from platinum residues, first evaporate the alcoholic solution to dryness, take up the residue in water, and pour the solution into caustic soda (sp. gr. 1.2), to which 8 per cent of glycerol * has been added.

* *Z. anal. Chem.*, **28**, 509.

Heat the liquid to boiling, which causes the platinum to be precipitated as a heavy black powder,

$$\underset{\text{Glycerol}}{2\,C_3H_8O_3} + 6\,H_2[PtCl_6] + 6\,H_2O = 36\,HCl + 2\,CO_2\uparrow + \underset{\text{Oxalic acid}}{2\,H_2C_2O_4} + 6\,Pt.$$

Wash the powder first with water, then with hydrochloric acid, and finally with water again. Dry, ignite (to destroy any of the organic compound), weigh and transform, as before, into chloroplatinic acid.

Reactions in the Dry Way

All platinum compounds, when heated with soda on charcoal, are reduced to the gray, spongy metal, which assumes a metallic luster on being rubbed with a pestle in an agate mortar. It can be distinguished from gold by its color, and from lead, tin, and silver by its infusibility and insolubility.

Separation of Gold from Platinum

Precipitate the platinum from a concentrated solution with a solution of ammonium chloride; filter and treat the solution with ferrous sulfate to precipitate the gold.

The separation may take place in the reverse order in some such way as follows: Evaporate the solution nearly to dryness and, in case nitric acid is present, add hydrochloric acid and evaporate again, repeating the operation if necessary. Then to the dilute solution from which all nitric acid has been removed and in which but little hydrochloric acid remains, add a slight excess of sodium oxalate and heat for some time: gold is precipitated and platinum remains dissolved. Filter, add ammonium chloride and evaporate almost to dryness. Treat the residual salts with alcohol which dissolves the sodium oxalate and ammonium chloride leaving behind ammonium chloroplatinate. If only a little platinum is present, evaporate the filtrate from the gold to dryness, ignite to destroy the oxalate, wash the residual platinum with water to dissolve sodium carbonate, dissolve the platinum in a little aqua regia, add ammonium chloride and continue as described above.

Analysis of Group II

Gold and platinum are two well-known metals which really belong to this group, but they are seldom present in large quantities in ordinary mineral analysis and the detection of small quantities is so important that it is customary to test for them separately as has been indicated (cf. pp. 282 and 287).

The metals of the second group are precipitated as sulfides by means of hydrogen sulfide in the presence of 0.3-normal mineral acid. The theory governing the precipitation of sulfides was discussed on pp. 13, 48, 153, 197, etc. In 0.3-normal mineral acid, the concentration of sulfur ions, formed by the ionization of hydrogen sulfide, is made so small that the solubility products of the sulfides of zinc, nickel, cobalt, iron and manganese are not reached unless large quantities of these elements are present in solution. In quantities up to 0.5 gm. of metal, zinc sulfide is the only one which is at all likely to precipitate in acid of this concentration, and then only when it is carried down with a considerable quantity of some second-group metal. The solubility-product of lead sulfide is about 4.2×10^{-28} and that of

cadmium sulfide is 3.6×10^{-29}, while that of zinc sulfide is 1.2×10^{-23}. Compared with *mercuric sulfide*, with its solubility-product of 4.0×10^{-53}, lead sulfide is quite soluble, but compared with zinc sulfide, it is much less soluble. In precipitating these sulfides there is some tendency for the sulfide precipitate to carry down with it some of the metals of the succeeding groups partly by adsorption, but this tendency is so slight that even with zinc the test is usually obtained in the proper place when as much as 2 mgs. are originally present.

The solubilities of the sulfides of the second group vary so greatly that it is possible to separate them from one another by regulating the acid concentration so that enough sulfur ions are furnished by hydrogen sulfide to precipitate one metal and not another. For the same reason, when hydrogen sulfide is passed into the acid solution, the most insoluble sulfide is precipitated first and very little, if any, of a more soluble sulfide is formed until the precipitation of the former is complete. In this respect the behavior of arsenic forms an apparent exception; but this is due, as already pointed out (p. 244), to the absence of an appreciable quantity of arsenic cations in the solution of an arsenate. The order in which the metals are precipitated as sulfides from cold solutions, as the acid concentration is progressively decreased, is approximately as follows: arsenic, mercury and copper; antimony, bismuth and stannic tin; cadmium, lead and stannous tin; zinc, iron, nickel, cobalt and manganese. It will be noticed that zinc is placed a little in front of nickel and cobalt in this arrangement. This is the proper order for the precipitation, but after the sulfides have been formed a short time, nickel and cobalt sulfides become less soluble than freshly-precipitated cadmium, lead or stannous sulfide.

The theory of the solution of the sulfides has also been indicated (pp. 153, 190). The more soluble sulfides can be dissolved by merely increasing the concentration of the hydrogen ion. Thus the sulfides of antimony, tin, lead, cadmium, etc., can be dissolved by treatment with concentrated hydrochloric acid. Heating the solution to expel hydrogen sulfide hastens the dissolving, but the most effective expedient is to add an oxidizing agent, which oxidizes the sulfide ions as fast as they are formed in solution. Thus even mercuric and arsenic sulfides will dissolve readily on being treated with aqua regia or with bromine water.

Two methods for analyzing this group of cations will be described. The first method is based upon the preliminary separation of *arsenic, antimony* and *tin* from *mercury, lead, bismuth, copper* and *cadmium* by taking advantage of the fact that the first three elements mentioned form sulfides which dissolve in **ammonium polysulfide** solution. The second method * is similar in principle except that by using **sodium polysulfide,** the sulfides of *mercury, arsenic, antimony* and *tin* are dissolved leaving behind the sulfides of *lead, bismuth, copper* and *cadmium* which do not dissolve, except in very small quantities, in either sodium polysulfide or in ammonium polysulfide.

Most of the sulfides of the copper group show a slight tendency to dissolve in either sodium or ammonium polysulfide. Thus 5 to 10 mgs. of CuS and 0.5 to 1.0 mgs. of HgS may dissolve in ammonium polysulfide. None of the sulfides, however, dissolve to any extent in ammonium monosulfide. In sodium polysulfide, of the concentration recommended, not more than 1 mg. of copper and bismuth sulfides dissolve under normal conditions; the other sulfides of the copper group are even less soluble in sodium polysulfide. The advantage of using sodium polysulfide lies in the fact that it accomplishes in most cases a cleaner separation of the tin group from the copper group.

* Cf. A. A. NOYES: *Qualitative Chemical Analysis*, eighth edition, 1920.

METHOD A

The sulfides of arsenic, antimony and tin dissolve readily in 6-normal ammonium polysulfide solution. It is easy to dissolve 0.5 gm. of arsenic either as As_2S_3 or as As_2S_5, 0.5 gm. of antimony as Sb_2S_5 or 0.5 gm. of tin as SnS_2 in either ammonium monosulfide or the polysulfide. Scarcely any SnS and only about 0.1 gm. of antimony as Sb_2S_3 will dissolve in 25 cc. of 6-normal ammonium monosulfide, but as much as 0.5 gm. of either SnS or Sb_2S_3 will dissolve in the same quantity of ammonium polysulfide. Ammonium monosulfide dissolves scarcely any of the sulfides of the other subgroup, so that when the antimony and tin are known to be present in the higher state of oxidation, it is advisable to use ammonium sulfide rather than the polysulfide for the separation of the two subgroups.

TABLE IX. — SEPARATION OF THE COPPER AND TIN GROUPS

METHOD A

Solution may contain: Hg^{++}, Pb^{++}, Bi^{+++}, Cu^{++}, Cd^{++}, As^{+++}, AsO_3^{---}, AsO_4^{---}, Sb^{+++}, Sb^{+++++}, SbO_4^{-}, Sn^{++}, Sn^{++++} and Groups III, IV and V. *Make the solution 0.3-normal with HCl and saturate with H_2S. Filter and examine the filtrate for Groups III, IV and V. Treat the precipitate with $(NH_4)_2S_x$.* (1)

Residue: HgS, PbS, Bi_2S_3, CuS, CdS. *Examine by Table X.* (2)	Solution: $[AsS_4]^{---}$, $[SbS_4]^{---}$, $[SnS_3]^{--}$. *Add HCl.* (3)	
	Precipitate: As_2S_5, Sb_2S_5, SnS_2, S. *Examine by Table XI.* (3)	Filtrate: NH_4Cl. *Reject.*

PROCEDURE

1. Add to the neutral solution 5 cc. of 6-normal hydrochloric acid and saturate with hydrogen sulfide in the cold. Filter promptly and wash with hot water containing hydrogen sulfide. Heat the filtrate to boiling and pass hydrogen sulfide into it for ten minutes to make sure that all arsenic will be precipitated. If a yellow precipitate is formed slowly by this treatment, filter it off through a new filter and evaporate the filtrate nearly to dryness. Then add 10 cc. of 12-normal hydrochloric acid, saturate the cold solution with hydrogen sulfide, heat nearly to boiling and again introduce hydrogen sulfide. Cool, dilute to 100 cc. and saturate again with hydrogen sulfide. Filter off the precipitate and examine the filtrate for the metals of Groups III, IV, and V (cf. p. 199 or 203). This repeated treatment with hydrogen sulfide is necessary when considerable arsenic is present (cf. p. 244).

2. Transfer the precipitated sulfides to a porcelain dish and add about 10 cc. of ammonium polysulfide (or, better, ammonium monosulfide if it is certain that the precipitate contains no stannous sulfide nor a large quantity of antimony trisulfide). Cover the dish and warm gently for a short time with frequent stirring. Dilute with a little water, filter and wash with hot water containing a little ammonium sulfide. If the original residue was large and the treatment with ammonium sulfide has evidently reduced its bulk, it is advisable to repeat the treatment with ammonium sulfide in order to make sure that all of the arsenic, antimony and tin sulfides have been converted into soluble thio salts. Examine the residue by the method outlined in Table X.

3. Dilute the ammonium sulfide extract with an equal volume of water, add hydrochloric acid until the stirred solution is acid to litmus, heat to boiling and filter as soon as the sulfides of arsenic, antimony and tin have settled. Reject the filtrate and examine the precipitate by the method outlined in Table XI.

TABLE X. — ANALYSIS OF THE COPPER GROUP

Residue from Table IX: HgS, PbS, Bi_2S_3, CuS, CdS. *Boil with 2-normal* HNO_3. (1)

Residue: HgS. *Dissolve in aqua regia or in bromine water. Dilute, filter off S, and test with* $SnCl_2$. *White precipitate of* Hg_2Cl_2 *(or* Hg_2Br_2*) or a gray precipitate of* Hg_2Cl_2 *(or* Hg_2Br_2*)+Hg shows presence of Hg.* (2)	Solution: Pb++, Bi+++, Cu++, Cd++. *Add 6-normal* H_2SO_4, *evaporate, dilute and filter.* (3)		
	Precipitate: $PbSO_4$. *Dissolve in* $NH_4C_2H_3O_2$ *solution and add* K_2CrO_4. *Yellow precipitate of* $PbCrO_4$ *shows presence of Pb.* (4)	Filtrate: Bi+++, Cu++, Cd++. *Add 6-normal* NH_4OH *in excess.* (5)	
		Precipitate: $Bi(OH)_3$. *Dissolve in HCl, concentrate the solution and pour it into considerable water. White precipitate of BiOCl indicates the presence of bismuth. Filter and add* Na_2SnO_2. *Black residue is Bi.* (6)	Solution: $[Cu(NH_3)_4]$++, $[Cd(NH_3)_4]$++. *A blue solution shows Cu. If in doubt, add* $HC_2H_3O_2$ *and* $K_4Fe(CN)_6$ *to a portion of the solution. Red precipitate shows Cu.* (7) *Decolorize the solution, if necessary, with KCN and test with* H_2S. *Yellow precipitate of CdS shows presence of Cd.* (8)

PROCEDURE

1. Treat the residue from the ammonium sulfide treatment (Table IX) with 2-normal nitric acid, boiling for a short time. Filter and wash with hot dilute nitric acid. Examine the filtrate by (3).

2. Transfer the residue, and a part of the filter if necessary, to a porcelain dish and digest with hot aqua regia, or warm with saturated bromine water. Boil off the excess of chlorine or bromine, but do not evaporate to dryness on account of the danger of losing some mercuric salt by volatilization. Dilute somewhat and filter. Sometimes, when the elements of the copper group are present in large quantity, the residue of sulfur (and filter paper) will contain metastannic acid. To recover the tin, digest the residue with bromine again if it is at all dark colored, filter and reject the filtrate. Then warm the residue with a little ammonium sulfide solution and add it to the solution obtained upon treatment of the original hydrogen sulfide precipitate with ammonium polysulfide (Table IX). Test the solution obtained by the above treatment with aqua regia, or bromine, for mercury by adding stannous chloride solution. *A white precipitate of* Hg_2Cl_2 *or* Hg_2Br_2 *shows that mercury is present.* The precipitate turns gray when an excess of stannous chloride is added (cf. p. 212).

3. To the filtrate obtained in (1) add 10 cc. of 6-normal sulfuric acid and evaporate in a porcelain dish until white fumes of sulfuric acid are evolved. The purpose of this treatment is to expel all nitric acid, in which lead sulfate is somewhat soluble.

Cool and pour into 10 cc. of water, rinsing out the dish with a little cold water. Stir well and let the solution stand five minutes but not much longer. Filter and treat the filtrate by (5). When much bismuth is present some basic bismuth sulfate is often precipitated with the lead sulfate, but the greater part of the bismuth will remain in solution, particularly if the water is kept cold. The basic bismuth sulfate, $(BiO)_2SO_4$, is more coarsely crystalline than lead sulfate. When such a precipitate is obtained, treat it with 10 cc. of hot, 6-normal hydrochloric acid, add 10 cc. of 6-normal sulfuric acid and evaporate as above. The precipitate of lead sulfate now obtained will be free from bismuth. The treatment of the first sulfate precipitate with hydrochloric acid will dissolve a part or all of the lead sulfate.

4. Dissolve the precipitate of lead sulfate by pouring small portions of hot 3-normal ammonium acetate solution through the filter. Do not use over 25 cc. of the acetate solution and wash once with hot water after each addition of the acetate. To the solution thus obtained add a few drops of potassium chromate solution and 2 to 5 cc. of 6-normal acetic acid. *A yellow precipitate of lead chromate, insoluble in acetic acid, shows the presence of lead.* Bismuth chromate is readily soluble in acetic acid.

5. Neutralize the filtrate obtained in (3) with ammonia, using a liberal excess. This serves to precipitate bismuth hydroxide and form soluble complex cations with copper and cadmium. If the original hydrogen sulfide precipitate was not washed thoroughly, a precipitate of ferric hydroxide or of aluminium hydroxide may be obtained at this point. Both of these precipitates have a different appearance than bismuth hydroxide and do not give the confirmatory test for bismuth. Examine the filtrate by (7).

6. Pour a little 6-normal hydrochloric acid through the filter containing the bismuth hydroxide and evaporate till only a few drops of liquid remain, or a moist residue. Add 1 or 2 cc. of water and pour into 100 cc. of hot water. After standing two or three minutes, filter off any BiOCl and wash once with cold water. Prepare a fresh solution of sodium stannite by taking a few drops of stannous chloride solution, diluting with 5 cc. of water and adding sodium hydroxide solution, a few drops at a time, until the $Sn(OH)_2$ which first forms redissolves. Pour this solution through the filter containing the BiOCl. *A black residue of bismuth* is obtained when this element is present (cf. p. 225).

7. If the ammoniacal filtrate from (5) is blue, *copper is present.* The only other element which is likely to be confused with copper at this point is nickel, which also forms a blue solution with ammonia. The color of the ammoniacal nickel solution is very much paler than that of the corresponding copper solution, and it is rare that enough nickel is left with the hydrogen sulfide precipitate, due to incomplete washing, to cause trouble. In cases of doubt, acidify a little of the ammoniacal solution with acetic acid and add one drop of potassium ferrocyanide solution. *A red precipitate of $Cu_2[Fe(CN)_6]$ is formed if copper is present.* The test is much more sensitive than the blue test with ammonia; nickel, under the same conditions, gives a less characteristic green precipitate.

(8) If the ammoniacal solution is blue, add potassium cyanide solution until it is colorless, or only a few drops if the solution is already colorless. Pass hydrogen sulfide into the solution for half a minute. *A yellow precipitate of cadmium sulfide is formed if cadmium is present.* A red precipitate of $(CSNH_2)_2$ may be formed if too much H_2S is added (p. 232).

Sometimes a small black precipitate is obtained in the cadmium test which is most likely due to a little mercury or lead that was not properly removed from the solution. In such cases, filter off the precipitate, wash it with water until free from

cyanide and boil gently for five to ten minutes in a covered dish with about 15 cc. of 1.2-normal sulfuric acid (6-normal acid diluted with four volumes of water). This serves to dissolve cadmium sulfide, but will not dissolve copper or mercury sulfides and should convert lead sulfide into lead sulfate. Filter, dilute with three times as much water and saturate with hydrogen sulfide. A yellow precipitate of cadmium sulfide will now be obtained if cadmium is present.

TABLE XI. — ANALYSIS OF THE ARSENIC-TIN GROUP

Precipitate from Table IX: As_2S_5, Sb_2S_5, SnS_2, S. *Warm with 12-normal HCl.* (1)

Residue: As_2S_5. *Dissolve in 6-normal HCl and $KClO_3$. Evaporate, dilute, neutralize with NH_4OH and add $MgCl_2 \cdot NH_4Cl$ solution. A white precipitate of $MgNH_4AsO_4$ indicates As. Dissolve in 6-normal HCl, and treat with H_2S. Yellow precipitate of As_2S_5 or As_2S_3 shows As.* (2)	Solution: $SbCl_4^-$, $SnCl_6^{--}$. *Evaporate to small volume, pour upon clean platinum foil, and place a clean piece of zinc in the solution; a black spot on the platinum indicates Sb. When the evolution of hydrogen has ceased, remove the zinc and, if any tin deposit adheres to the platinum, rub it off and dissolve it, with the remaining zinc, in a small test-tube in one or two drops of concentrated hydrochloric acid. Dilute with water and add a few drops of mercuric chloride solution. A white or gray precipitate shows Sn is present.* (3)

PROCEDURE

1. Transfer the sulfides of arsenic, antimony and tin, which are mixed with considerable free sulfur, to a porcelain dish and digest for about fifteen minutes with 12-normal hydrochloric acid. Heat gently, but do not boil hard. This serves to dissolve antimony pentasulfide (forming antimony trichloride which unites with HCl to form $HSbCl_4$) and stannic sulfide (forming stannic chloride which forms H_2SnCl_6 with HCl) but does not dissolve much, if any, arsenic pentasulfide. Dilute with a little water and filter. Treat the solution by (3).

2. Heat the residue of arsenic sulfide with 15 cc. of 6-normal hydrochloric acid and add powdered potassium chlorate from time to time in small portions. When all the yellow sulfide has dissolved, dilute somewhat and filter off the residual sulfur. Evaporate the solution to about 2 cc., add 6-normal ammonia in considerable excess and a few drops of magnesium-ammonium chloride reagent. If no precipitate forms at once, stir vigorously and rub the inside walls of the glass vessel with the stirring rod and let the solution stand at least an hour. If a precipitate of magnesium ammonium arsenate, $MgNH_4AsO_4$, forms, pour off the liquid through a filter and dissolve the precipitate in 10 cc. of 6-normal hydrochloric acid. Saturate the solution with hydrogen sulfide, heat to boiling and again introduce hydrogen sulfide for at least five minutes. *A yellow precipitate of arsenic sulfide will form if as much as 1 mg. of arsenic is present.*

3. Evaporate the solution of $HSbCl_4$ and H_2SnCl_6, obtained in (1), to a very small volume and pour a few drops of the concentrated solution upon a piece of clean platinum foil. Place a small piece of bright zinc in the liquid so that it comes in contact with both solution and platinum. After a few seconds, take away the zinc and notice whether a *coal black spot of antimony* has formed upon the platinum. Mercury and copper if present will also be precipitated upon the platinum, but the mercury deposit is gray and the copper deposit is red. The antimony spot is insoluble in sodium hypochlorite solution (cf. pp. 250, 264).

Réplace the zinc upon the platinum foil and allow the action to continue until there is no more evolution of hydrogen. Then rinse carefully with distilled water, taking care not to disturb the contact of the zinc with the platinum. Take away the zinc and carefully remove any tin that may adhere to the platinum. Dissolve the mixture of tin and zinc in one or two drops of concentrated hydrochloric acid. Dilute the solution in a very small test-tube with a little water and add a few drops of mercuric chloride solution. *A white precipitate of mercurous chloride which usually turns gray shows the presence of tin.*

SUPPLEMENTARY PROCEDURES

Analysis of Arsenic-Tin Group

A. If the sulfide precipitate, obtained by acidifying the ammonium polysulfide solution, consists chiefly of arsenic pentasulfide, it is best to dissolve the arsenic sulfide first by means of ammonium carbonate solution (p. 245). Then the residue of Sb_2S_5, SnS_2 and S can be examined for antimony and tin.

To detect the arsenic in the ammonium carbonate solution, add hydrochloric acid, which reprecipitates arsenic pentasulfide. Dissolve the sulfide as indicated in Table XI and confirm the arsenic test as described there.

B. An excellent method for separating antimony and tin is based upon the fact that antimony trisulfide is less soluble than the sulfides of tin. To accomplish the separation, proceed as follows:

Dissolve the sulfides of antimony and tin as described above in exactly 10 cc. of 12-normal hydrochloric acid; when there is no further evolution of hydrogen sulfide gas, dilute with 3 cc. of water and filter with the aid of suction. Dilute the filtrate to exactly 55 cc. and transfer the solution to a small flask. Place the flask in a beaker of boiling water and introduce hydrogen sulfide into the solution in the flask for ten minutes but no longer. Filter and wash the precipitate with hot water.

An orange precipitate of antimony trisulfide will be formed when only 1 mg. of Sb is present. Dissolve the precipitate in a little 12-normal hydrochloric acid, evaporate nearly to dryness, dilute and test with platinum and zinc as described above.

The filtrate from the Sb_2S_3 can be used for the tin test. Instead of reducing the tin with zinc, metallic lead can be used (p. 269). Evaporate the solution to about 3 cc., but not to dryness on account of the danger of losing stannic chloride by volatilization, add 10 cc. of water, 10 gms. of granulated lead and heat gently for ten minutes. Pour the hot solution through the filter into 10 cc. of 0.2-normal mercuric chloride. Filter off any mercurous chloride that may be precipitated, dissolve any adhering lead chloride by washing with hot water and, if not already blackened, add ammonia to the precipitate (cf. p. 213).

Analysis of Group II according to A. A. Noyes

METHOD B

Noyes places mercuric mercury in the arsenic-tin group by using sodium polysulfide * instead of ammonium polysulfide for treating the original precipitate of sulfides in the filtrate from Group I.

* The reagent recommended is 3-normal in Na_2S, 1-normal in Na_2S_2 and 1-normal in NaOH. Dissolve 16 g. S, 480 g. $Na_2S \cdot 9\,H_2O$ and 20 g. NaOH per liter of water. The solution may also be prepared as follows: Digest 16 g. S and 20 g. NaOH with 1 liter of 4-normal NaOH solution prepared by saturating 500 cc. of 4-normal NaOH solution with H_2S and then diluting with an equal volume of 4-normal NaOH.

TABLE XII.—SEPARATION OF THE COPPER AND TIN GROUPS

METHOD B

Solution may contain cations of all the metals except silver and mercurous mercury. *Make the solution 0.3-normal in HCl and saturate with H_2S. Filter and examine the filtrate for Groups III, IV and V. Treat the precipitate with Na_2S_2 solution.* (1)

Residue: PbS, Bi_2S_3, CuS, CdS. *Examine by Table XI.* (2)	Solution: $[HgS_2]^{--}$, $[AsS_4]^{---}$, $[SbS_4]^{---}$, $[SnS_3]^{--}$. *Add HCl.* (3)	
	Precipitate: HgS, As_2S_5 Sb_2S_5 SnS_2, S. (4)	Filtrate: NaCl. *Reject.*

PROCEDURE

1. Precipitate, filter and wash the sulfides of this group as in Method A (p. 289, 1).

2. Transfer the precipitated sulfides to a porcelain dish and add 3 to 10 cc. of sodium polysulfide solution. Cover the dish and heat gently for a short time with constant agitation. Dilute with 10 cc. of water, filter and wash with hot water. Examine the residue by the method outlined in Table XIII.

3. Add hydrochloric acid to the sodium sulfide extract until the stirred solution is acid to litmus, then add 1 cc. more of 6-normal acid. Shake well and filter. If the precipitate is all sulfur, as can be determined by comparing the color with that produced by adding 5 cc. of 6-normal acid to 3 cc. of sodium sulfide reagent diluted with 7 cc. of water, it is unnecessary to test for mercury, arsenic, antimony or tin. (In case of doubt, transfer the precipitate to a casserole and heat a short time with 8 cc. of 6-normal NH_4OH; this dissolves arsenic sulfide readily and also small quantities of antimony and tin sulfide. Filter and note that if mercury is present the residue will consist of *black* HgS and sulfur, together with possibly small quantities of brownish-black Bi_2S_3 and CuS. Unless the dark color is apparent there is no need of testing further for mercury. To the ammoniacal filtrate, add 5 drops of $(NH_4)_2S$ reagent, heat to boiling and filter if necessary. Add 10 cc. of water, acidify with hydrochloric acid and shake well; the presence of arsenic, antimony, and tin will be shown by the color of any precipitated sulfide, but it is necessary to remember that a mixture of antimony and tin sulfides gives a brown color in many cases.) Reject the filtrate and examine the precipitate, produced by adding hydrochloric acid to the sodium sulfide solution, by the method outlined in Table XIV.

TABLE XIII. — ANALYSIS OF THE COPPER GROUP

METHOD B

Residue from Table XII: PbS, Bi_2S_3, CuS, CdS. *Boil with 3-normal HNO_3 and filter.* (1)

Residue: S usually contaminated with negligible quantities of sulfides. *Reject.*	Solution: Pb++, Bi+++, Cu++, Cd++. *Add H_2SO_4*, evaporate, dilute and filter. (2)			
	Precipitate: $PbSO_4$. *Examine as in Method A.* (2)	Filtrate: Bi+++, Cu++, Cd++. Add NH_4OH in excess and filter. (3)		
		Precipitate: $Bi(OH)_3$. *Add Na_2SnO_2.* Black residue is Bi. (4)	Filtrate: $[Cd(NH_3)_4]$++.	$[Cu(NH_3)_4]$++,
			A blue solution shows Cu. *If in doubt, add $HC_2H_3O_2$ and $K_4[Fe(CN)_6]$ to a small portion.* Red precipitate is $Cu_2[Fe(CN)_6]$. (5)	*To the larger part of the solution add H_2SO_4 and Fe. Filter and saturate the filtrate with H_2S.* Yellow precipitate shows Cd. (6)

PROCEDURE

1. Treat the residue from the sodium sulfide treatment (Table XII) with 5-15 cc. of 3-normal nitric acid. After boiling for a few minutes, filter and reject the residue unless it is desired to test for less than 2 mg. of mercury in the presence of considerable copper and cadmium. In that case examine it as described in Table XIV, 3.

2. Test for lead exactly as in Method A (Table X).

3. Neutralize the filtrate from the lead sulfate, and add enough ammonia to make the solution smell strongly. Filter, if necessary, examine the precipitate by (4) and the filtrate by (5).

4. Wash the precipitate of $Bi(OH)_3$ thoroughly. Prepare some sodium stannite solution by taking a few drops of stannous chloride, diluting with 5 cc. of water and adding to the *cold* solution enough sodium hydroxide to dissolve the stannous hydroxide which first forms. Pour this solution through the filter containing the $Bi(OH)_3$. *A black residue confirms the bismuth test.*

5. A blue ammoniacal solution indicates the presence of copper. To confirm this conclusion, and to test for copper when there is not enough present to color the ammoniacal solution, add acetic acid and potassium ferrocyanide to a part of the ammoniacal filtrate of § 4. A red precipitate shows that copper is present. A white precipitate indicates that cadmium is probably present.

6. To the larger part of the ammoniacal filtrate from the bismuth hydroxide precipitation, add sulfuric acid until an acid reaction is obtained and then add 5 cc. of 6-normal sulfuric acid in excess. Heat the mixture to about 60° and, if any

copper is present, shake two minutes with about 0.5 g. of iron powder. Filter and reject the residue of iron and copper. Dilute the filtrate with 25 cc. of water and saturate with hydrogen sulfide. *A yellow precipitate of cadmium sulfide is obtained if cadmium is present.*

TABLE XIV. — ANALYSIS OF THE ARSENIC-TIN GROUP

METHOD B

Precipitate from Table XII: HgS, As_2S_5, SnS_2, S. *Heat with* 12-*normal HCl.* (1)

Residue: HgS, As_2S_5, S. *Add* NH_4OH. (2)		Solution: $HSbCl_4$, H_2SnCl_6. Dilute, heat and saturate with H_2S. (5)	
Residue: HgS, S. *Add HCl and* $KClO_3$. *Test for mercury with* $SnCl_2$ *as in Method A.* (3)	Solution: AsS_4^{---}, $AsSO_3^{---}$. *Evaporate almost to dryness, add* HNO_3, *evaporate again and add* NH_4OH. *Filter if necessary, and add* $Mg(NO_3)_2$. A white precipitate should be $MgNH_4AsO_4$. *Filter, wash the precipitate with a little water and add* $AgNO_3$ *and* $HC_2H_3O_2$ *to it.* Red residue of Ag_3AsO_4 shows As is present. (4)	Precipitate: Sb_2S_3. *Dissolve in HCl and add metallic tin.* A black deposit insoluble in NaBrO shows the presence of Sb. (6)	Solution: H_2SnCl_6. *Partly neutralize and test with* H_2S. *Evaporate without filtering and boil with metallic antimony. Test for stannous tin with* $HgCl_2$. A white or gray precipitate shows Sn is present. (7).

PROCEDURE

1. Transfer the sulfide precipitate (drained as dry as possible by suction) to a test tube and heat it in boiling water for 10 minutes with 10 cc. of 12-normal hydrochloric acid. Then introduce hydrogen sulfide into the hot solution for 1 minute, slowly add 3 cc. of water while stirring and filter through a dry filter, using suction. The filter should be placed upon a smaller hardened filter and should be fitted closely to the funnel. Wash the residue first with 6-normal HCl and then with hot water. Examine the filtrate of $HSbCl_4$ and H_2SnCl_6 by § 5 and the residue for arsenic and mercury by § 2.

2. Warm and stir the residue with about 10 cc. of 6-normal ammonium hydroxide which dissolves the arsenic and does not affect the mercuric sulfide. Filter and wash this residue with dilute ammonium hydroxide. Examine the filtrate for arsenic by § 4.

3. Digest the residue of mercuric sulfide and excess of sulfur with 5 cc. of hydrochloric acid and a little potassium chlorate. Boil until the odor of chlorine disappears, dilute to 15 cc. and test for mercury with stannous chloride as in Method A.

4. Evaporate the ammoniacal solution of ammonium thioarsenate and arsenate nearly to dryness. This causes some of the arsenic to precipitate as sulfide but in a condition such that it is oxidized by 6-normal nitric acid to arsenic acid. To the concentrated solution obtained by evaporation, add 5 cc. of 6-normal nitric acid and

boil until the residue is all dissolved or only a little sulfur remains. Evaporate nearly to dryness, add 3 cc. of ammonium hydroxide and filter if necessary. The arsenic is now present as ammonium arsenate. To the clear solution add magnesium nitrate reagent,* stir vigorously and allow the test to stand for some time. A white crystalline precipitate of magnesium ammonium arsenate shows that arsenic is present. Filter, wash the precipitate with a little water and pour over it a mixture of 1 cc. silver nitrate solution and 6 drops acetic acid. A dark red residue of silver arsenate confirms the conclusion that arsenic is present.

5. Dilute the solution from (2) with water to a volume of 55 cc., and saturate with hydrogen sulfide at about 90°. Pass the hydrogen sulfide through the hot solution for eight minutes, to precipitate antimony sulfide, Sb_2S_3. Filter and wash the precipitate with hot water. Test the filtrate for tin by § 7.

6. Transfer the antimony sulfide precipitate to a small casserole, dissolve it in 5 cc. of concentrated hydrochloric acid, heating if necessary. Unless a clear solution is obtained, add 5 cc. of water and filter, rejecting the residue. Evaporate the filtrate to about 2 cc., cool and add a flat piece of bright, mossy tin. After 10 minutes pour off the liquid, wash the metal in water and examine it for a *black* † residue of antimony. Pour upon it about 2 cc. of freshly-prepared sodium hypobromite solution.‡ Antimony, unlike arsenic, is undissolved by this treatment.

7. As a preliminary test to see whether any tin is likely to be present, add just 4 cc. of concentrated ammonium hydroxide to the filtrate from § 5 and saturate with hydrogen sulfide. If no precipitate forms after 10 minutes, it is unnecessary to test further for tin. In case a precipitate is obtained, evaporate, without filtering, to a volume of 15 cc. or farther if the sulfide has not dissolved. Add about 2 g. of powdered antimony and boil gently for 2 minutes. Filter and add at once 2 cc. of hydrochloric acid and a little mercuric chloride solution. A white or gray precipitate proves that tin is present.

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* Dissolve 75 g. of $Mg(NO_3)_2$ in 500 cc. of 6-normal nitric acid and 502 cc. of 6-normal ammonium hydroxide. This provides enough ammonium salt to prevent any precipitation of $Mg(OH)_2$ with ammonia and should leave the solution ammoniacal.

† A deposit of copper may be obtained here but is red or brown in color.

‡ Add NaOH solution, drop by drop, to 2 cc. of saturated bromine water until the solution becomes colorless or yellow, then add as many drops more of sodium hydroxide solution.

GROUP I. HYDROCHLORIC ACID GROUP

To this group belong silver, mercury (in mercurous compounds), lead, thallium, and (under some circumstances) tungsten.

SILVER, Ag. At. Wt. 107.88

Sp. Gr. = 10.5 M. Pt. = 961° C.

Occurrence. — Silver occurs both native and combined (chiefly with sulfur, arsenic, and antimony).

Of the silver-bearing minerals the following may be mentioned: horn silver, AgCl; argentite, Ag_2S; pyrargyrite, Ag_3SbS_3; and proustite, Ag_3AsS_3. Silver is also found with tetrahedrite, and with galena.

Metallic silver is of a pure white color. It absorbs oxygen in the molten state, which it gives up (with tiny explosions) on cooling.

The proper solvent for silver is nitric acid. It is insoluble in dilute hydrochloric and sulfuric acids, but dissolves readily in boiling sulfuric acid, with evolution of sulfur dioxide:

$$2\,Ag + 2\,H_2SO_4 = 2\,H_2O + SO_2\uparrow + Ag_2SO_4.$$

The solubility of silver in concentrated sulfuric acid is utilized in separating silver from gold and platinum in alloys.

Silver forms three oxides: silver suboxide, Ag_4O; silver oxide, Ag_2O; silver peroxide, Ag_2O_2. Of these oxides, Ag_2O alone is a basic anhydride; only one series of salts is known.

Silver peroxide is formed at the anode during the electrolysis of a concentrated, aqueous solution of silver nitrate. The grayish-black crystalline powder has the composition: $Ag_4O_4 = Ag_2O \cdot Ag_2O_3$.*

Silver oxide, Ag_2O, is a brownish-black powder, which on being heated to 300° is completely decomposed into metal and oxygen.

Most of the silver salts are colorless; the following, however, are colored: the bromide (pale yellow), the iodide (yellow), the sulfide (black), the phosphate (yellow), the arsenite (yellow), the arsenate (brown), the ferricyanide (orange), and the chromate (reddish-brown). Most of the salts are insoluble in water, and are blackened on exposure

* BRAUMER and KUZMA, *Ber.*, **1907**, 3371. It may be regarded as the silver salt of the hypothetical argentic acid, $HAgO_2$; its symbol could then be written $Ag[AgO_2]$, analogous to the aurates, e.g., $K[AuO_2]$.

to the light. The nitrate, chlorate, perchlorate, fluoride, nitrite, sulfate, and acetate are soluble in hot water.

Reactions in the Wet Way

1. **Potassium** and **Sodium Hydroxides** precipitate brown silver oxide,

$$2\,Ag^+ + 2\,OH^- \rightarrow H_2O + \mathbf{Ag_2O},$$

insoluble in an excess of the precipitant, but readily soluble in nitric acid and in ammonia. If the solution in ammonia is allowed to stand, black fulminating silver (chiefly AgN_3) is deposited.

2. **Ammonia.** — If a neutral solution of a silver salt is cautiously treated with ammonia, the first drops produce a white precipitate, which changes quickly to the brown oxide, Ag_2O. The greater part of the silver, however, remains in solution as complex silver-ammonia salt; even the oxide is dissolved by an excess of ammonia:

$$\mathbf{Ag_2O} + 4\,NH_3 + H_2O \rightarrow 2\,[Ag(NH_3)_2]^+ + 2\,OH^-.$$

3. **Sodium Carbonate** precipitates white silver carbonate, which becomes yellow on being boiled, being slightly decomposed into oxide. with loss of carbon dioxide:

$$2\,Ag^+ + CO_3^{--} \rightarrow \mathbf{Ag_2CO_3};$$

$$\mathbf{Ag_2CO_3} \rightarrow \mathbf{Ag_2O} + CO_2\uparrow.$$

4. **Ammonium Carbonate** produces the same precipitate, but it is soluble in an excess of this reagent.

5. **Sodium Phosphate** throws down in neutral silver solutions a yellow precipitate of silver phosphate:

$$3\,Ag^+ + 2\,HPO_4^{--} \rightarrow H_2PO_4^- + \mathbf{Ag_3PO_4}.$$

Silver phosphate is easily soluble in nitric acid and in ammonia. The solubility of the phosphate in ammonia is due to the formation of complex silver-ammonia ions.

$$\mathbf{Ag_3PO_4} + 6\,NH_3 \rightarrow 3\,[Ag(NH_3)_2]^+ + PO_4^{---}.$$

By neutralizing the ammoniacal solution with nitric acid, or the nitric acid solution with ammonia, the silver phosphate is reprecipitated.

6. **Hydrochloric Acid** or **Soluble Chlorides** precipitate white, curdy silver chloride from neutral and acid solutions:

$$Ag^+ + Cl^- \rightarrow \mathbf{AgCl}.$$

Silver chloride is appreciably soluble in pure water (cf. p. 21), particularly on boiling, but it is quite insoluble if an excess of silver nitrate or of hydrochloric acid is present (cf. p. 20).

Silver chloride dissolves to a considerable extent in a large excess of hydrochloric acid or of alkali chloride, due to the formation of complex anions, $[AgCl_3]^{--}$, but it is much less soluble in dilute nitric acid.

It is very soluble in ammonia,

$$AgCl + 2\,NH_3 \rightarrow [Ag(NH_3)_2]^+ + Cl^-,$$

but is reprecipitated on addition of nitric acid to this solution:

$$[Ag(NH_3)_2]^+ + 2\,H^+ + Cl^{--} \rightarrow 2\,NH_4^+ + AgCl.$$

Silver chloride is also readily soluble in potassium cyanide solution,

$$AgCl + 2\,CN^- \rightarrow [Ag(CN)_2]^- + Cl^-,$$

and if such a solution is acidified, silver cyanide will be precipitated;

$$[Ag(CN)_2]^- + H^+ \rightarrow HCN + AgCN.$$

In the absence of acid, silver chloride is also readily soluble in a solution of sodium thiosulfate:

$$2\,AgCl + 3\,S_2O_3^{--} \rightarrow [Ag_2(S_2O_3)_3]^{==} + 2\,Cl^-.$$

On boiling this solution, silver sulfide is precipitated slowly if considerable $Na_2S_2O_3$ is present, but more quickly upon diluting.

It is evident that the solubility in all the above cases is due to the formation of complex ions containing silver (cf. p. 25).

Silver chloride is slowly attacked by boiling, concentrated sulfuric acid, with evolution of hydrochloric acid, and the formation of crystalline silver sulfate, insoluble in sulfuric acid.

By boiling with caustic soda or caustic potash solution, silver chloride is only partially decomposed; in the cold it is unaffected. Sodium carbonate solution does not affect it; but by fusing with sodium carbonate it is completely decomposed:

$$4\,AgCl + 2\,Na_2CO_3 = 4\,NaCl + 2\,CO_2\uparrow + O_2\uparrow + 4\,Ag.$$

By fusing silver chloride itself a yellow liquid is obtained, which on cooling solidifies to a vitreous mass; it may be removed from the crucible by treatment with zinc and dilute sulfuric acid (see below) mass.

7. **Potassium Iodide** precipitates yellow, curdy silver iodide, practically insoluble in ammonia, but easily soluble in potassium cyanide and sodium thiosulfate solutions.

The $[Ag(NH_3)_2]^+$ cation furnishes more Ag^+ cations than silver iodide in contact with water, but the $[Ag(CN)_2]^-$ and $[Ag_2(S_2O_3)_3]^{==}$ are much more stable complexes and furnish less Ag^+ cations than silver iodide does.

8. **Ferrous Sulfate** precipitates gray metallic silver from boiling solutions:

$$Ag^+ + Fe^{++} \rightarrow Fe^{+++} + Ag.$$

Frequently a basic ferric salt is precipitated at the same time, particularly from very dilute solutions.

Ferrous sulfate added to an ammoniacal-tartrate solution of a silver salt also causes the formation of a gray precipitate which may be

silver suboxide, Ag_4O, or a mixture of finely divided silver mixed with some organic substance.

9. **Zinc,** having a greater solution pressure than silver, precipitates the latter from neutral solutions. Similarly, if insoluble silver chloride is covered with dilute sulfuric acid and a piece of zinc placed in contact with the chloride, the latter will be reduced to metal.

$$2\,\mathbf{AgCl} + \mathbf{Zn} = Zn^{++} + 2\,Cl^- + \mathbf{2\,Ag}.$$

10. **Hydrogen Sulfide** precipitates from neutral, ammoniacal, and acid solutions black silver sulfide,

$$2\,Ag^+ + H_2S \rightarrow 2\,H^+ + \mathbf{Ag_2S}.$$

insoluble in ammonia, alkali sulfides, and dilute potassium cyanide solution. Silver sulfide is so insoluble (cf. p. 21) that enough Ag^+ ions are present in aqueous solutions containing $[Ag(NH_3)_2]^+$ or even $[Ag(CN)_2]^-$ to exceed the solubility product of Ag_2S when in contact with slightly ionized hydrogen sulfide. Silver sulfide is, however, perceptibly soluble in a concentrated solution of potassium cyanide, and easily soluble in hot dilute nitric acid (cf. p. 190).

11. **Ammonium Thioacetate** also precipitates silver sulfide from acid solutions:

$$2\,Ag^+ + C_2H_3OS^- + H_2O \rightarrow \mathbf{Ag_2S} + HC_2H_3O_2 + H^+.$$

12. **Sodium Thiosulfate** precipitates white silver thiosulfate soluble in an excess of the reagent but from the boiling solution silver sulfide is reprecipitated.

$$2\,Ag^+ + S_2O_3^{--} \rightarrow \mathbf{Ag_2S_2O_3}.$$

$$\mathbf{Ag_2S_2O_3} + 2\,S_2O_3^{--} \rightarrow [Ag_2(S_2O_3)_3]^{----}.$$

$$[Ag_2(S_2O_3)_3]^{----} + 2\,H^+ \rightarrow \mathbf{Ag_2S} + 2\,S + H_2O + SO_4^{--} + 2\,SO_2\uparrow.$$

The presence of a little acid favors the precipitation of the sulfide in accordance with the last reaction.

13. **Potassium Chromate** precipitates brownish-red silver chromate soluble in ammonia and in nitric acid:

$$2\,Ag^+ + CrO_4^{--} \rightarrow \mathbf{Ag_2CrO_4}.$$

14. **Potassium Dichromate** precipitates reddish-brown silver dichromate soluble in ammonia and in nitric acid:

$$2\,Ag^+ + Cr_2O_7^{--} \rightarrow \mathbf{Ag_2Cr_2O_7}.$$

Reactions in the Dry Way

Fused with soda on charcoal, all silver compounds yield a white, malleable, metallic button without incrustation (difference from lead and tin), readily soluble in nitric acid (difference from tin). The

solution is not precipitated by very dilute sulfuric acid, but is immediately precipitated by hydrochloric acid (difference from lead).

The reactions of lead and mercurous compounds have already been described (pp. 213, 219).

Analysis of Group I

Silver, lead and mercurous chlorides are difficultly soluble in water. According to the table on page 21, 0.038 mg. Hg_2Cl_2, 0.015 mg. AgCl and about 1 gm. $PbCl_2$ will dissolve in 100 cc. of water. From these values, it is evident that the precipitation of mercurous and silver cations will be nearly complete from 100 cc. of solution and that, although lead chloride is much less soluble in a solution containing an excess of chlorine ions than it is in water, lead will never be precipitated completely as chloride from aqueous solutions. By the addition of a large excess of alcohol, however, the precipitation of lead chloride can be made nearly complete, but the addition of alcohol at this stage of the analysis is rarely permissible except in the analysis of certain alloys or compounds rich in lead.

Lead chloride is characterized by the fact that it is much more soluble in hot water than in cold. On dissolving lead compounds in a small quantity of hydrochloric acid, the chloride often separates out as the solution cools, and in such cases it is easier to remove the lead chloride at this stage of the analysis than to precipitate it as sulfide, dissolve in nitric acid and reprecipitate as sulfate.

As group precipitant either hydrochloric acid or ammonium chloride can be used. Any other soluble chloride would accomplish the same end but would interfere more with the subsequent analysis. If the solution is originally alkaline, the addition of hydrochloric acid may cause the formation of some other precipitate. Thus an alkaline cyanide solution, a solution of thio salt in ammonium sulfide and an alkaline silicate solution will usually give precipitates upon the addition of any acid. Such precipitates often dissolve upon the addition of a little more acid and cause no trouble, but sometimes it is best to treat the precipitate as an insoluble substance by the methods described in Part IV.

Bismuth, antimony and stannic chlorides on being diluted with water are changed into insoluble basic salts. These precipitates may be filtered off and dissolved by repeatedly passing a little 2-normal hydrochloric acid through the filter. Then, as the solution thus obtained is likely to contain lead chloride, it is best to evaporate to about 1 cc., dilute with 25 cc. of water and precipitate with hydrogen sulfide without paying any attention to the formation of a basic salt upon diluting: such basic salts are changed by hydrogen sulfide to less soluble sulfides.

TABLE XV. — ANALYSIS OF THE SILVER GROUP

Solution may contain all the metals. *Add 6-normal HCl, filter and examine the filtrate for succeeding groups. Treat with hot water.* (1)

Residue: AgCl, Hg_2Cl_2. *Pour ammonia through the filter.* (3)	Solution: Pb++. *Test for lead with H_2SO_4. Filter off $PbSO_4$ and treat the precipitate with hot $NH_4C_2H_3O_2$ solution. Add K_2CrO_4; a yellow precipitate of $PbCrO_4$ shows presence of Pb.* (2)
Residue: $Hg(NH_2)Cl+Hg$.	Solution: $[Ag(NH_3)_2]+$. *Add HNO_3: white precipitate shows the presence of Ag.* (4)

The analysis of the first group of metals is based upon the solubility of lead chloride in hot water, the solubility of silver chloride in ammonia, and the blackening of mercurous chloride by ammonia.

PROCEDURE

1. To the cold, concentrated solution add 6-normal hydrochloric acid and, if a precipitate is formed, continue adding hydrochloric acid, drop by drop, until no further precipitation takes place. Filter through a small filter (cf. p. 61) and wash the precipitate four times with a little cold water, blowing a fine stream from the wash bottle around the upper edge of the filter and waiting each time until the filter has drained before adding a fresh portion of water. Do not use more than 5 cc. of water each time. Take the entire filtrate for the analysis of Groups II, III, IV and V. Pour a little hot water through the filter. Test the residue by (3).

2. Test the first 5 cc. portion of hot water that runs through the filter for lead by adding a few drops of concentrated sulfuric acid. If a precipitate forms, filter, wash once with cold water and then pour 10 cc. of hot 3-normal ammonium acetate solution through the filter. Add a few drops of potassium chromate solution to the solution and 3 cc. of 6-normal acetic acid. A yellow precipitate of lead chromate should form if *lead is present*. Continue washing the chlorides with hot water until 5 cc. of the washings will give no test for lead with potassium chromate solution.

(3) Pour 5 cc. of 6-normal ammonia around the upper edge of the filter, catching it, as it runs through the funnel, in a test-tube. Acidify the filtrate with nitric acid. A white, curdy precipitate of silver chloride is formed when *silver is present*. The treatment with ammonia causes any mercurous chloride to turn black on the filter (cf. p. 213).

If considerable mercurous chloride and very little silver chloride is present, the treatment with ammonia may fail to dissolve silver chloride. In such a case, wash the black residue and pour repeatedly a mixture of 3 cc. 6-normal hydrochloric acid and 10 cc. of saturated bromine water through the filter. This serves to convert the mercurous chloride to soluble mercuric salt and leaves the silver on the filter as silver chloride or bromide. Wash the filter with hot water and again pour 5 cc. of ammonium hydroxide through it and test the ammoniacal solution for silver with nitric acid.

PART III. REACTIONS OF THE ACID CONSTITUENTS OR ANIONS

DIVISION OF THE ACIDS INTO GROUPS

The classification of the acids which is given here was first published by R. Bunsen in 1878 (in manuscript form) for the use of his students; it was adopted (with his consent) by V. Meyer and F. P. Treadwell in their "Tabellen zur qualitativen Analyse." It is based upon the different solubilities of the barium and silver salts.

Group I

Acids whose silver salts are insoluble in water and in nitric acid, but whose barium salts are soluble in water.

To this group belong hydrochloric, hydrobromic, hydriodic, hydrocyanic, ferrocyanic, ferricyanic, cobalticyanic, thiocyanic, and hypochlorous acids.

Group II

Acids whose silver salts are soluble in nitric acid, but are insoluble, or difficultly soluble, in water, and whose barium salts are soluble in water.

To this group belong hydrosulfuric (hydrogen sulfide), hydroselenic, hydrotelluric, nitrous, acetic, cyanic, hypophosphorous and hydrazoic acids.

Group III

Acids whose silver salts are white and soluble in nitric acid, but whose barium salts are difficultly soluble or insoluble in water, but soluble in nitric acid.

To this group belong sulfurous, selenous, tellurous, phosphorous, carbonic, oxalic, iodic, boric, molybdic (selenic and telluric), tartaric, citric, meta- and pyrophosphoric acids.

Group IV

Acids whose silver salts are colored and soluble in nitric acid, but whose barium salts are insoluble in water and soluble in nitric acid.

To this group belong phosphoric, arsenic, arsenious, vanadic, thiosulfuric, chromic, and periodic acids.

Group V

Acids whose silver and barium salts are soluble in water.

To this group belong nitric, chloric, perchloric, persulfuric and the manganic acids.

Group VI

Acids whose silver salts are soluble in water, but whose barium salts are insoluble in nitric acid.

To this group belong sulfuric, hydrofluoric, and fluosilicic acids.

Group VII

Non-volatile acids, which form soluble salts only with the alkalies.

To this group belong silicic, tungstic, titanic, niobic, tantalic, and zirconic acids

GROUP I

Silver Nitrate produces a precipitate insoluble in nitric acid.
Barium Chloride causes no precipitation.

HYDROCHLORIC ACID, HCl

Occurrence. — Hydrochloric acid is found free in nature, but in small quantities (for example, in the exhalations of active volcanoes); its salts, however, are exceedingly common, especially those with the alkalies. (See these.)

Preparation. — Hydrochloric acid is set free by the action of concentrated sulfuric acid upon a chloride. Ordinary rock salt is usually used, it being the cheapest chloride.

If sulfuric acid is allowed to act upon ordinary salt, a considerable evolution of hydrochloric acid takes place even in the cold, with the formation of sodium bisulfate:

$$NaCl + H_2SO_4 = NaHSO_4 + HCl\uparrow.$$

And, on warming, the sodium bisulfate reacts with more sodium chloride:

$$NaHSO_4 + NaCl = Na_2SO_4 + HCl\uparrow.$$

When only one hydrogen of a dibasic acid is replaced by metal, the resulting salt is usually designated by placing the prefix *bi* before the name of the anion; sodium bicarbonate, $NaHCO_3$; sodium bisulfate, $NaHSO_4$, etc. There is *twice* as much acid per equivalent of base as in the case of the normal salt.

Hydrochloric acid may be prepared by dropping concentrated sulfuric acid into 12-normal hydrochloric acid. It is also formed by the action of water on many acid chlorides:

$$PCl_3 + 3\,H_2O = H_3PO_3 + 3\,HCl.$$

Properties. — Hydrochloric acid is a colorless gas, with a suffocating odor, which forms dense clouds in moist air. It is readily soluble in water (one volume of water dissolves, at 18° C., 451 volumes of hydrochloric acid). The specific gravity of the saturated, aqueous solution is 1.21, and 100 cc. of this solution contain 50.7 gms. of hydrochloric acid gas. The concentrated hydrochloric acid of the laboratory is about 12-normal, and contains 36 to 38 per cent of the gas by weight. As regards its behavior on evaporation, see page 60. The

aqueous solution of hydrochloric acid is one of our strongest acids. In dilute solution it is almost entirely ionized,

$$HCl \rightleftarrows H^+ + Cl^-,$$

and such a solution is a good conductor of electricity.

The behavior of hydrochloric acid on oxidation is characteristic; water is formed and chlorine is set free:

$$4\,HCl + O_2 \rightleftarrows 2\,H_2O + 2\,Cl_2.$$

This oxidation will not take place on exposure to atmospheric, or even pure, oxygen, but only by strong oxidizing agents such as:

The peroxides of the heavy metals, all nitrates, nitrites, chlorates, hypochlorites, chromates, selenates, and *tellurates.*

The peroxides of the light metals do not yield chlorine, but hydrogen peroxide:

$$BaO_2 + 2\,HCl = BaCl_2 + H_2O_2.$$

1. Oxidation of Hydrochloric Acid by Means of Peroxides

(*a*) *By manganese dioxide:*

$$4\,HCl + MnO_2 = 2\,H_2O + MnCl_2 + Cl_2\uparrow.$$

The manganese is reduced from the quadrivalent to the bivalent condition and the negatively charged chlorine atom becomes neutral chlorine gas. Thus one atom of manganese oxidizes two atoms of chlorine.

Some other acid, preferably sulfuric, can be used to combine with the manganese and then the yield of chlorine from a given quantity of hydrochloric acid will be twice as large:

$$MnO_2 + 2\,HCl + H_2SO_4 = MnSO_4 + 2\,H_2O + Cl_2\uparrow.$$

(*b*) *By lead peroxide:*

$$4\,HCl + PbO_2 = 2\,H_2O + PbCl_2 + Cl_2\uparrow.$$

(*c*) *By chromium trioxide:*

$$2\,CrO_3 + 12\,HCl = 6\,H_2O + 2\,CrCl_3 + 3\,Cl_2.$$

2. Oxidation of Hydrochloric Acid by Nitric Acid, etc.

When concentrated nitric acid acts upon concentrated hydrochloric acid, the products of the reaction are water, nitrosyl chloride and free chlorine:

$$HNO_3 + 3\,HCl = 2\,H_2O + NOCl + Cl_2.$$

In this reaction the valence of the nitrogen has been reduced from five to three, and two atoms of chlorine have been oxidized to form an electrically neutral chlorine molecule.

A mixture of one molecule of nitric acid with three of hydrochloric acid is known as

Aqua Regia. — The acids are usually mixed, not according to their weights, but according to their volumes.

Aqua regia is, therefore, chlorine water, with the distinction that the chlorine exists in the nascent state; which explains why aqua regia is a much more energetic reagent than ordinary chlorine water. Nitrous acid, chloric acid, hypochlorous acid, selenic and telluric acids all react similarly with hydrochloric acid.

Hydrochloric acid is *monobasic;* its salts are called *chlorides.*

Solubility of Chlorides

Nearly all chlorides are soluble in water, but the following are insoluble: mercurous chloride, Hg_2Cl_2; silver chloride, AgCl; cuprous chloride, Cu_2Cl_2; lead chloride, $PbCl_2$; thallium chloride, TlCl; aurous chloride, AuCl; platinous chloride, $PtCl_2$; bismuth oxychloride, BiOCl; antimony oxychloride, SbOCl; mercuric oxychloride, Hg_2Cl_2O.

All these chlorides which are insoluble in water are more soluble in strong hydrochloric acid.

Aurous chloride and platinous chloride dissolve readily in aqua regia, as a result of being oxidized, but silver chloride is not very soluble even in aqua regia.

By boiling the insoluble chlorides with a concentrated solution of sodium carbonate, all, with the exception of silver chloride, are readily decomposed, e.g.:

$$\mathbf{Hg_2Cl_2} + Na_2CO_3 = 2\,NaCl + CO_2\uparrow + \mathbf{Hg_2O}.$$

By filtration, a chloride solution is obtained which is free from heavy metal.

By fusing with sodium carbonate, even silver chloride is decomposed,

$$4\,AgCl + 2\,Na_2CO_3 = 4\,NaCl + 2\,CO_2\uparrow + O_2\uparrow + 4\,\mathbf{Ag},$$

and silver chloride may also be decomposed by treatment with metals and dilute acid (cf. p. 301).

The deliquescent chlorides (lithium, calcium, and strontium) are all soluble in absolute alcohol and in amyl alcohol.

The chlorides of sodium and barium are quite insoluble in concentrated hydrochloric acid; they can, therefore, be easily separated from other chlorides which are soluble in water by saturating the solution with hydrochloric acid gas.

Almost all chlorides are insoluble in ether, with the exception of mercuric, stannous, stannic, auric, and ferric chlorides.

Reactions of Chlorides in the Wet Way

A neutral solution of an alkali chloride should be used for these reactions. All chlorides except those of mercury and cadmium are quite completely ionized in aqueous solution, so that it is a matter of indifference which chloride we take for the following reactions, provided there is no independent reaction taking place due to the presence of the cation.

1. **Dilute Sulfuric Acid** (1 : 10) produces no reaction, even on warming.

2. **Concentrated Sulfuric Acid** decomposes the solid chloride almost completely in the cold, completely on warming. Sulfate and colorless hydrochloric acid gas result from this reaction; and the latter is easily recognized by its odor, by the clouds which it forms in moist air or with ammonia vapors (obtained by holding a glass rod wet with ammonia near the test-tube), and by its turning moist blue litmus-paper red. Water is not made turbid by hydrochloric acid (difference from fluosilicic acid).

Silver chloride and mercurous chloride are decomposed with difficulty by sulfuric acid, the latter with evolution of sulfur dioxide; the *mercurous* sulfate (which is at first formed) is oxidized (at the expense of the oxygen of the sulfuric acid) to *mercuric* sulfate:

$$(a)\ Hg_2Cl_2 + H_2SO_4 = Hg_2SO_4 + 2\,HCl;$$

$$(b)\ Hg_2SO_4 + 2\,H_2SO_4 = 2\,HgSO_4 + 2\,H_2O + SO_2\uparrow.$$

If a chloride and an oxidizing agent are heated with concentrated sulfuric acid, free chlorine is evolved (cf. p. 307).

3. **Phosphoric Acid,** heated with a chloride, similarly causes the evolution of hydrochloric acid gas. If an oxidizing agent is present at the same time, chlorine gas is evolved.

4. **Silver Nitrate** produces a white, curdy precipitate of silver chloride,

$$Cl^- + Ag^+ \rightarrow \mathbf{AgCl},$$

insoluble in nitric acid, soluble in ammonia, potassium cyanide, and sodium thiosulfate solutions. (See Silver.)

From a solution of silver chloride in ammonia, acids reprecipitate silver chloride. From a solution in potassium cyanide, acids precipitate silver cyanide. If it is desired to test a solution of ferrous sulfate for the presence of a small amount of chloride, it must be strongly acidified with nitric acid, as otherwise a precipitate of metallic silver will be obtained, which may cause confusion (cf. p. 300). The best

way to test the solution of ferrous sulfate for hydrochloric acid is to add sodium carbonate solution until alkaline, boil, and filter. In the filtrate the acids originally present are now in the form of their sodium salts, in the presence of an excess of sodium carbonate; the solution should be made acid with nitric acid before the silver nitrate is added.

The detection of chlorine when present in the form of chloride of a heavy metal is accomplished in a similar manner; and, with the exception of silver chloride, any insoluble chloride may be decomposed in the same way, by boiling with sodium carbonate solution.

In order to detect the presence of chlorine in silver chloride, treat it with dilute sulfuric acid and zinc (p. 301), after a short time pour off the solution from the deposited silver and test it with silver nitrate.

Or, fuse the silver chloride with sodium carbonate, extract the melt with water, filter, acidify with nitric acid, and test with silver nitrate.

5. **Potassium Dichromate and Sulfuric Acid.** — If a dry chloride is mixed with potassium dichromate, covered with concentrated sulfuric acid, and the mixture heated in a small retort, brownish vapors are given off which condense, in the receiver, to a brown liquid (chromyl chloride, CrO_2Cl_2):

$$K_2Cr_2O_7 + 4\,NaCl + 6\,H_2SO_4 = 3\,H_2O + 4\,NaHSO_4 + 2\,KHSO_4 + 2\,CrO_2Cl_2.$$

Chromyl chloride is an acid chloride, and is, therefore, decomposed by water into chromic and hydrochloric acids:

$$CrO_2Cl_2 + 2\,H_2O = H_2CrO_4 + 2\,HCl.$$

On adding caustic soda or potash, an alkali chloride and a yellow alkali chromate are obtained. If the solution is then acidified, some ether and a little hydrogen peroxide added, and the liquid shaken, the upper ether layer will be colored blue, showing the presence of chromium; and the presence of chromium indicates that a chloride was originally present (difference from bromide and iodide).

6. **Potassium Permanganate** oxidizes a chloride in acid solution. On the other hand, hydrobromic and hydriodic acids are oxidized much more readily than hydrochloric acid.

7. **Mercurous Nitrate** and **Lead Acetate** give precipitates of mercurous chloride and lead chloride. From auric chloride solution, lead acetate precipitates a double chloride of lead and gold.

Behavior of Chlorides on Ignition

The chlorides of the alkalies and alkaline earths melt (without perceptible decomposition) on being heated in the air. The chlorides of the sesquioxides are decomposed, more or less completely, on being

ignited in the air. Thus, ferric chloride is almost quantitatively decomposed into ferric oxide, with loss of chlorine:

$$4\,FeCl_3 + 3\,O_2 = 2\,Fe_2O_3 + 6\,Cl_2\uparrow.$$

In the presence of hydrochloric acid, or ammonium chloride, ferric chloride may be volatilized completely without any decomposition.

The chlorides of gold and of the platinum metals are readily decomposed into chlorine and metal:

$$2\,AuCl_3 = 2\,Au + 3\,Cl_2\uparrow;$$
$$PtCl_4 = Pt + 2\,Cl_2\uparrow.$$

The remaining chlorides are mostly volatile, without perceptible decomposition except in the case of ammonium chloride (cf. p. 96).

Detection of Chlorine in Non-electrolytes

Besides uniting with metals and with hydrogen, chlorine also forms compounds with the metalloids; e.g., PCl_3, PCl_5, $AsCl_3$, $AsCl_5$, $SbCl_3$, $SbCl_5$, CCl_4, $SiCl_4$, etc.

All these compounds, which may be regarded as acid chlorides, are decomposed by water with the formation of hydrochloric acid, which can be tested for in the usual way. The hydrolysis usually takes place at the ordinary temperatures. Thus, phosphorus trichloride yields with water phosphorous acid and hydrochloric acid,

$$PCl_3 + 3\,HOH = H_3PO_3 + 3\,HCl,$$

and phosphorus pentachloride yields phosphoric acid and hydrochloric acid:

$$PCl_5 + 4\,HOH = H_3PO_4 + 5\,HCl.$$

The remaining acid chlorides are decomposed in a similar way by water at the ordinary temperature, with the exception of carbon tetrachloride, which is decomposed by water only by heating in a closed tube:

$$CCl_4 + 2\,H_2O = CO_2 + 4\,HCl.$$

Chlorine acts upon a great many hydrocarbons, forming substitution-products which are non-electrolytes, and consequently will not give the chloride tests; for example, if chloroform, $CHCl_3$, is shaken with a solution of aqueous silver nitrate, it will not yield a precipitate of silver chloride. In order to test such compounds for chlorine (as is frequently necessary in the study of organic compounds), the chlorine must be changed to hydrochloric acid by one of the following methods:

1. **Carius' Method.** — By heating the compound in a sealed glass tube with concentrated nitric acid, in the presence of silver nitrate, the compound is completely decomposed; all the chlorine is changed to silver chloride, which can be filtered off, and, after treatment with zinc and dilute sulfuric acid, can be tested as above. The precautions to be taken in sealing and opening the tube are described in Vol. II.

2. **By Heating with Lime.** — Place a layer of granular lime (free from chloride) then a mixture of the substance to be tested and lime, and finally another layer of lime in a small glass tube, which should be about 25 cm. long and about 1 cm. wide. By gently tapping the tube, open up a canal between the upper wall of the tube and the substance, through which the gases evolved may escape. Place the tube horizontally in a small combustion furnace and heat (first the front layer of lime, then the back layer, and finally the entire contents of the tube) to a dull red heat. By this means the organic substance will be completely decomposed, and the chlorine will be found combined with the lime in the form of calcium chloride. Cool, dissolve the contents of the tube in dilute nitric acid, filter off the carbon and test the filtrate with silver nitrate for chlorine ions.

3. **Treatment with Sodium.** — Place a small amount of the dry substance to be tested in a small test-tube, add a small piece of sodium (freed from petroleum), and cover the metal with another layer of the substance. Heat the tube in the gas-flame; the decomposition takes place suddenly with incandescence. Place the hot tube and its contents in a small beaker containing water (which breaks the tube); sodium chloride dissolves with other sodium compounds. Filter the solution, make acid with nitric acid, and test with silver nitrate for halogens.

Free Chlorine

Chlorine, whether produced by the oxidation of hydrochloric acid or by igniting certain chlorides, is a greenish-yellow gas, with a suffocating odor. It is absorbed by water (one volume of water absorbs at 10° C. about 2.7 volumes of chlorine gas), forming chlorine water, a yellowish-green liquid, and a poor conductor of electricity (although better than pure water, showing that some ions are present). Chlorine decomposes water to a slight extent, forming hydrochloric acid and hypochlorous acid:

$$H_2O + Cl_2 \rightleftarrows 2\,H^+ + Cl^- + ClO^-.$$

In this reaction one atom of chlorine is oxidized to a positive valence of one and another atom of chlorine is reduced to a negative valence of one (cf. p. 179). This reaction, as the application of the mass-action law indicates, is favored by the presence of hydroxyl ions and hindered by the presence of hydrogen ions. If, besides water, which is only slightly ionized, dilute alkali is present, the reaction takes place quantitatively from left to right.

$$Cl_2 + 2\,OH^- \rightarrow Cl^- + ClO^- + H_2O.$$

The decomposition of chlorine water takes place slowly in the dark, but more rapidly in the light, and in the presence of oxidizable substances. The bleaching action of chlorine water depends upon its oxidizing power.

Chlorine water is a strong oxidizing agent.

If a solution of potassium iodide is treated with chlorine water, iodine is set free, and the solution turns yellow to brown:

$$2\,KI + Cl_2 = 2\,KCl + I_2.$$

If the yellow solution is shaken with carbon disulfide, or chloroform, a more highly colored, violet, non-aqueous solution of iodine is obtained (cf. p. 17). By the addition of more chlorine water the solution becomes colorless, owing to the oxidation of the iodine to colorless iodic acid:

$$I_2 + 6\,H_2O + 5\,Cl_2 = 10\,HCl + 2\,HIO_3.$$

The free iodine can also be detected by the addition of some starch paste (instead of carbon disulfide, etc.), which is turned blue by iodine.

1. **Silver Nitrate** gives a white precipitate of silver chloride when added to chlorine water; this precipitation, however, is not quantitative, for one-sixth of the chlorine is changed into soluble silver chlorate:

$$3\,Cl_2 + 5\,Ag^+ + 3\,H_2O = 5\,\mathbf{AgCl} + ClO_3^- + 6\,H^+.$$

On adding a slight excess of sulfurous acid to chlorine water, the chlorine is readily and completely changed into hydrochloric acid:

$$Cl_2 + H_2O + H_2SO_3 = H_2SO_4 + 2\,HCl.$$

From this solution the chlorine can be precipitated quantitatively by a silver solution.

Chlorine may also be easily changed into the form of a chloride by the action of ammonia (cf. p. 174).

$$3\,Cl_2 + 8\,NH_3 \rightarrow 6\,NH_4Cl + N_2\uparrow.$$

Chlorine can be changed to a chloride by the action of hydrogen peroxide in the presence of sodium or potassium hydroxide:

$$Cl_2 + 2\,OH^- + H_2O_2 \rightarrow 2\,H_2O + 2\,Cl^- + O_2\uparrow.$$

2. **Metallic Mercury** is attacked by chlorine at ordinary temperatures, forming insoluble mercurous chloride.

$$\mathbf{Hg_2} + Cl_2 = \mathbf{Hg_2Cl_2}.$$

If therefore chlorine water is shaken with metallic mercury until it no longer smells of chlorine, a neutral solution is obtained which contains no free chlorine. If hydrochloric acid is present, the solution now reacts acid, and gives a precipitate with silver nitrate, for metallic mercury is not attacked by hydrochloric acid. This reaction is used as a test for hydrochloric acid in the presence of chlorine.

3. **Metallic Zinc** also reacts with chlorine water,

$$\mathbf{Zn} + Cl_2 \rightarrow Zn^{++} + 2\,Cl^-.$$

4. **Indigo Solution** is decolorized by chlorine water. If a dilute solution of indigo is used, the discharge of the color is a sensitive test for chlorine.

5. **Iodo-starch Paper** (paper which has been dipped in starch paste containing potassium iodide) is turned blue by chlorine. The test is also delicate when starch paste containing zinc iodide in solution is used.

HYPOCHLOROUS ACID, HOCl

Hypochlorous acid in the free state is unknown. Its anhydride, Cl_2O, is a deep yellow gas at ordinary temperatures and has an unpleasant, irritating odor. It explodes into chlorine and oxygen on being heated. Dilute aqueous solutions of hypochlorous acid can be distilled. The acid is very weak and has the ionization constant of 3.7×10^{-8} at 17°.

Preparation. — A solution of free hypochlorous acid is obtained by shaking chlorine water with yellow mercuric oxide until the solution no longer smells of chlorine:

$$2\,\mathbf{HgO} + 2\,Cl_2 + H_2O = (\mathbf{HgCl})_2\mathbf{O} + 2\,HOCl.$$

Brown, insoluble mercuric basic chloride is formed by the reaction, and the solution contains hypochlorous acid. If the solution is poured off from the insoluble basic mercuric salt and distilled, a pure solution of hypochlorous acid will be obtained; which, however, cannot be kept long in the light, for it decomposes into hydrochloric acid and oxygen:

$$2\,HOCl \rightarrow 2\,HCl + O_2\uparrow.$$

Hypochlorous acid is a vigorous bleaching agent; litmus and indigo are quickly decolorized.

The alkali salts of hypochlorous acid (hypochlorites) are obtained by neutralizing the acid with dilute sodium or potassium hydroxide; or more conveniently, by the action of chlorine on a dilute caustic alkali solution:

$$Cl_2 + 2\,OH^- = Cl^- + ClO^- + H_2O.$$

The ammonium salt cannot be prepared except at very low temperatures, because the nitrogen of ammonia is so readily oxidized (cf. p. 174).

All hypochlorites are readily changed, on warming, into chlorate * and chloride (cf. p. 179):

$$3\,KClO \rightarrow 2\,KCl + KClO_3,$$

consequently hypochlorites must always be prepared in cold, dilute solution.

* In the presence of 40 per cent or more of caustic potash, the potassium hypochlorite on being heated decomposes into chloride with evolution of oxygen and the formation of no chlorate (F. WINTELER, *Z. angew. Chem.*, **33** (1902), p. 778).

The most important commercial hypochlorite is the so-called "chloride of lime," which is obtained by passing chlorine gas over lime at the ordinary temperature.

Reactions in the Wet Way

All hypochlorites are soluble in water, and are decomposed by acids (even carbonic acid).

1. **Hydrochloric Acid** is oxidized by hypochlorites with evolution of chlorine:

$$ClO^- + Cl^- + 2\,H^+ \rightarrow H_2O + Cl_2\uparrow.$$

The reaction is favored by the presence of hydrogen ions. The reverse reaction is favored by the presence of hydroxyl ions (cf. p. 312).

2. **Sulfuric Acid** decomposes hypochlorites, setting free hypochlorous acid:

$$NaOCl + H_2SO_4 = NaHSO_4 + HOCl,$$

and carbonic acid acts similarly though less energetically.

$$2\,NaOCl + H_2CO_3 = Na_2CO_3 + 2\,HOCl.$$

It is due to the fact that hypochlorites are so readily decomposed with the formation of chlorine that they act as strong bleaching agents, indigo solution (a solution of indigo in sulfuric acid) being immediately decolorized.

Hypochlorites act as oxidizing agents not only in acid solutions, but also in alkaline solutions at ordinary temperatures (difference from chlorates), many metallic hydroxides being oxidized by them to higher hydroxides. Thus, ferrous hydroxide is readily oxidized to reddish-brown ferric hydroxide:

$$2\,Fe(OH)_2 + ClO^- + H_2O \rightarrow Cl^- + 2\,Fe(OH)_3,$$

and similarly lead, manganous, nickelous, and cobaltous hydroxides are oxidized to brownish-black hydroxides.

Less than 1 mg. of hypochlorite can be detected by boiling with lead acetate solution:

$$Pb^{++} + ClO^- + H_2O \rightarrow PbO_2 + 2\,H^+ + Cl^-.$$

If a peroxide is likely to be present, the solution must first be acidified with acetic acid before applying the test (cf. p. 90).

3. **Iodo-Starch Paper** is turned blue by hypochlorites in weakly alkaline solutions, owing to the separation of iodine:

$$2\,KI + NaOCl + H_2O = 2\,KOH + NaCl + I_2.$$

$$2\,I^- + ClO^- + H_2O \rightleftarrows Cl^- + 2\,OH^- + I_2.$$

The extent to which the reaction takes place depends upon the concentration of the hydroxyl ion; only in dilute alkali will enough iodine be formed to produce the blue coloration with the starch.

4. **Metallic Mercury.** — If a solution containing free hypochlorous acid is shaken with metallic mercury, brown basic mercuric chloride is formed, insoluble in water, but soluble in hydrochloric acid:

$$2\,Hg + 2\,HOCl = (HgCl)_2O + H_2O.$$

Under these same conditions free chlorine forms, on being shaken with mercury, white mercurous chloride, which is insoluble in hydrochloric acid.

This property is utilized in detecting hypochlorous acid in the presence of free chlorine. The mixture is shaken with mercury until a little of the solution no longer turns iodo-starch paper blue; the liquid is then carefully poured off, hydrochloric acid is added to the residue, and the mixture is shaken, when the basic chloride produced by hypochlorous acid goes into solution:

$$(HgCl)_2O + 2\,HCl = H_2O + 2\,HgCl_2,$$

while mercurous chloride remains undissolved.

If hydrogen sulfide is passed into the filtered solution, the formation of mercuric sulfide shows that hypochlorous acid was originally present.

The *salts* of hypochlorous acid behave differently toward mercury: they form insoluble mercuric oxide and a soluble chloride:

$$Hg + NaOCl = HgO + NaCl.$$

5. **Silver Nitrate** causes in solutions of hypochlorites an incomplete precipitation of silver chloride. One-third of the chlorine remains in solution in the form of chlorate:

$$3\,ClO^- + 2\,Ag^+ \rightarrow ClO_3^- + 2\,AgCl.$$

Hypochlorous acid is distinguished from chlorine by its behavior toward mercury; from hydrochloric acid by its oxidizing action; and from chloric acid by its being partly precipitated by silver nitrate, and by its oxidizing action in alkaline solutions.

6. **Permanganate** solution is not decolorized by hypochlorous acid. Litmus and indigo are decomposed slowly in alkaline solution and more rapidly decolorized in the presence of acid. If a solution of arsenious acid is colored blue by indigo, the latter is not bleached until the arsenious acid has been all oxidized to arsenic acid.

7. **Manganous Chloride.** — A saturated solution of $MnCl_2$ in concentrated hydrochloric acid gives a brownish black coloration owing to the formation of $MnCl_3$. Cf. p. 491.

HYDROBROMIC ACID, HBr

Occurrence. — Bromine compounds are always found in nature together with chlorine compounds; thus salts of hydrobromic acid are found in the ocean and in many mineral waters.

Preparation. — Hydrobromic acid is formed by the action of sulfuric acid upon a bromide:

$$2\,NaBr + H_2SO_4 = Na_2SO_4 + 2\,HBr.$$

But the hydrobromic acid obtained by means of this reaction is never pure, being contaminated with bromine; a part of the hydrobromic acid is oxidized by the sulfuric acid:

$$2\,HBr + H_2SO_4 \rightarrow 2\,H_2O + SO_2\uparrow + Br_2\uparrow.$$

The more concentrated the sulfuric acid used, the larger will be the yield of bromine.

If dilute sulfuric acid ($3\,H_2SO_4 : 1\,H_2O$) is used, the hydrobromic acid obtained is nearly free from bromine.

Pure hydrobromic acid may be obtained by the action of an acid bromide upon water:

$$PBr_3 + 3\,HOH = H_3PO_3 + 3\,HBr.$$

Properties. — Hydrobromic acid (like hydrochloric acid) is a colorless gas with a suffocating odor, having the property of fuming in moist air and forming clouds of ammonium bromide with vapors of ammonia. It is very soluble in water. The concentrated solution has the sp. gr. 1.78 and contains 82 per cent by weight of hydrobromic acid. Hydrobromic acid is less stable than hydrochloric acid and more stable than hydriodic acid.

Although hydrochloric acid can be kept in aqueous solution for an indefinitely long time, a solution of hydrobromic acid soon turns brown, owing to the separation of bromine. Hydrobromic acid is oxidized by atmospheric oxygen:

$$4\,HBr + O_2 = 2\,H_2O + 2\,Br_2\uparrow.$$

Owing to the slight solubility of cuprous bromide, and aided by the presence of a little free bromine, hydrobromic acid will dissolve copper, although this element is below hydrogen in the electromotive series (cf. pp. 41 and 227).

Hydrobromic acid is readily oxidized with separation of bromine,

by peroxides, nitrates, chromates, etc., provided a concentrated solution of hydrobromic acid is used.

Hydrobromic acid is a monobasic acid; its salts are called bromides. It is one of the strongest acids and the aqueous solutions are ionized to the same extent as solutions of hydrochloric acid.

The solubility of a bromide is similar to that of the corresponding chloride.

Reactions in the Wet Way

1. **Dilute Sulfuric Acid** (1 : 10) evolves no hydrobromic acid from bromides in the cold, but, on warming, does so from bromides of the alkalies.

2. **Concentrated Sulfuric Acid** causes evolution of hydrobromic acid and bromine from all bromides:

$$H_2SO_4 + 2\,Br^- \rightarrow SO_4^{--} + 2\,HBr$$

and

$$H_2SO_4 + 2\,HBr \rightarrow 2\,H_2O + SO_2\uparrow + Br_2\uparrow.$$

The solution is brown, and, on warming, yellowish-brown vapors are given off (difference from hydrochloric acid); which, as they contain hydrobromic acid, fume in moist air, have a suffocating odor, and do not render water turbid (difference from fluosilicic acid).

3. **Phosphoric Acid** causes the evolution of hydrobromic acid. If an oxidizing agent is also present, bromine is evolved.

4. **Silver Nitrate** produces a curdy, yellowish precipitate of silver bromide, insoluble in nitric acid, but soluble in ammonia, potassium cyanide, and sodium thiosulfate. Silver bromide is less soluble than silver chloride.

If, therefore, silver chloride is digested with potassium bromide, the former will be changed into silver bromide:

$$\mathbf{AgCl} + KBr = \mathbf{AgBr} + KCl.$$

If, however, silver bromide is heated and treated with chlorine gas, it is readily changed into silver chloride:

$$2\,\mathbf{AgBr} + Cl_2 = 2\,\mathbf{AgCl} + Br_2\uparrow.$$

5. **Chlorine Water,** on being added to solutions of soluble bromides, sets free bromine, which is soluble in carbon disulfide or chloroform, forming a brown solution; but it is changed, by an excess of chlorine water, into yellowish chloride of bromine (BrCl) (difference from iodine).

6. **Potassium Dichromate,** in the presence of dilute sulfuric acid, does not cause separation of bromine from aqueous solutions of bro-

mides; on shaking the solution with carbon disulfide, the latter remains colorless (difference from iodine).

7. **Potassium Dichromate and Concentrated Sulfuric Acid.** — On mixing a solid bromide with solid potassium dichromate, covering the mixture with concentrated sulfuric acid and distilling, a brown distillate is obtained (as with a chloride), which, however, consists of bromine and contains no chromium:

$$Cr_2O_7^{--} + 6\,Br^- + 14\,H^+ \rightarrow 2\,Cr^{+++} + 7\,H_2O + 3\,Br_2\uparrow .$$

On adding dilute sodium hydroxide to the distillate, a colorless (or sometimes a faint yellow) solution is obtained; which, after being acidified with sulfuric acid, does not give the chromium reaction with dilute sulfuric acid and hydrogen peroxide, but merely turns brown owing to the liberation of free bromine (difference from chlorine).

8. **Potassium Permanganate** oxidizes hydrobromic acid more readily than it does hydrochloric acid and less readily than it does hydriodic acid.

9. **Nitrous Acid** does not cause the separation of bromine from a dilute bromide solution in the cold (difference from iodine).

Detection of Bromine in Non-electrolytes

The method of procedure is exactly the same as was given in the case of chlorine in a non-electrolyte (see p. 311).

FREE BROMINE

Free bromine (which may be obtained by the oxidation of hydrobromic acid) is a brown liquid at the ordinary temperature, and dissolves in water, forming a colored solution. Bromine boils at 63°, and evaporates rapidly at ordinary temperatures. Bromine vapors are brownish red and very poisonous. The cold, saturated solution of bromine contains 2 to 3 per cent of dissolved bromine. Concentrated hydrochloric acid at the ordinary temperatures dissolves much more bromine; the saturated solution containing about 13 per cent of the substance is an efficient oxidizing agent. Alcohol, ether, carbon bisulfide, carbon tetrachloride and chloroform dissolve bromine very readily. Bromine is so much more soluble in these last three solvents, which are heavier than water and do not mix with it to any extent, that the greater part of the bromine can be removed by shaking the aqueous solution with a much smaller volume of the other liquid solvent. Bromine water, like chlorine water, is decomposed by standing in the light; by shaking with mercury the free bromine is taken up and the presence of hydrobromic acid is shown by the acid reaction.

Bromine, like chlorine, acts as a strong bleaching agent (oxidizing the color) and combines directly with metallic mercury, forming insoluble mercurous bromide.

The detection of hydrobromic acid in the presence of bromine is accomplished in precisely the same way as was described for the detection of hydrochloric acid in the presence of free chlorine (cf. p. 313).

Bromine acts upon solutions of alkali hydroxides exactly as chlorine does:

(*a*) In a cold dilute solution:

$$Br_2 + 2\,OH^- = Br^- + BrO^- + H_2O.$$

(*b*) On warming:

$$3\,Br_2 + 6\,OH^- \rightarrow 5\,Br^- + BrO_3^- + 3\,H_2O.$$

(*c*) Upon ammonia:

$$3\,Br_2 + 8\,NH_3 \rightarrow 6\,NH_4Br + N_2\uparrow.$$

HYDRIODIC ACID, HI

Occurrence. — Iodine occurs in nature as the iodide and as the iodate; most frequently as the former, accompanying (in small amounts) chlorine and bromine; e.g., in the ocean, in mineral waters, etc.

Preparation. — Hydriodic acid may be obtained pure by the action of an acid iodide upon water:

$$PI_3 + 3\,H_2O = H_3PO_3 + 3\,HI.$$

If we attempt to prepare hydriodic acid by the action of sulfuric acid upon iodides, even from dilute solutions, it is more difficult than in the case of hydrobromic acid to obtain a pure product, on account of the strong reducing power of hydriodic acid. The hydriodic acid thus obtained always contains a large amount of iodine, together with the reduction products of sulfuric acid, the latter varying in composition according to the concentration of the acid employed and of the iodide solution. Thus, with considerable concentrated sulfuric acid, sulfur dioxide is obtained:

$$2\,NaI + 3\,H_2SO_4 \rightarrow 2\,NaHSO_4 + 2\,H_2O + SO_2\uparrow + I_2.$$

But if considerable iodide is present, the sulfuric acid is reduced to sulfur and finally to hydrogen sulfide.

$$6\,KI + 7\,H_2SO_4 \rightarrow 6\,KHSO_4 + S + 4\,H_2O + 3\,I_2,$$

$$8\,KI + 9\,H_2SO_4 \rightarrow 8\,KHSO_4 + H_2S\uparrow + 4\,H_2O + 4\,I_2.$$

Properties. — Hydriodic acid is a colorless gas, with a suffocating odor; it fumes in moist air, and is readily soluble in water, forming a strongly fuming liquid of sp. gr. 1.99–2.10. The aqueous solution of hydriodic acid is even more difficult to keep than a solution of hydrobromic acid; it soon turns brown, owing to the separation of iodine:

$$4\,HI + O_2\,(air) \rightarrow 2\,H_2O + 2\,I_2.$$

If hydrogen sulfide is conducted into the brown solution, it is decolorized, with separation of sulfur:

$$I_2 + H_2S = 2\,HI + S.$$

Owing to the extremely slight ionization of complex mercuric iodide anions, hydriodic acid is capable of dissolving mercury, which is con-

siderably below hydrogen in the electromotive series (cf. pp. 10 and 41).

$$Hg + 4\,HI = [HgI_4]H_2 + I_2\uparrow.$$

Hydriodic acid (like hydrochloric and hydrobromic acids) is oxidized by peroxides, nitrates, nitrites, chromates, etc., with separation of iodine; in this case the oxidation of the hydriodic acid takes place so readily that a very dilute solution is oxidized by nitrous and chromic acids even in the cold.

Hydriodic acid is a monobasic acid; its salts are called iodides. It is a strong acid and the dilute aqueous solutions are almost completely ionized.

The solubilities of the iodine compounds are analogous to the corresponding bromine and chlorine compounds. The cuprous, silver, mercury and palladium salts are much less soluble than the corresponding chlorine or bromine compounds.

Reactions in the Wet Way

1. **Dilute Sulfuric Acid** (1 : 10) attacks the iodides of the alkalies perceptibly, but only on warming.

2. **Concentrated Sulphuric Acid** reacts in the cold (cf. p. 321).

3. **Silver Nitrate** produces a yellow, curdy precipitate of silver iodide, insoluble in nitric acid, and only slightly soluble in ammonia, but readily soluble in potassium cyanide and sodium thiosulfate.

Treatment with ammonia causes the silver iodide to assume a much lighter color.

By the action of chlorine gas, silver iodide is readily changed into silver chloride:

$$2\,AgI + Cl_2 = 2\,AgCl + I_2.$$

On the other hand, if chloride or bromide of silver is treated with potassium iodide solution it will be changed into silver iodide:

$$AgCl + KI = KCl + AgI,$$
$$AgBr + KI = KBr + AgI.$$

This apparently anomalous behavior is easy to explain. As its position in the electromotive series shows, free chlorine can displace bromine or iodine in its salts; it has a greater tendency to be reduced to chloride ions. On the other hand, silver iodide is far less soluble than silver bromide and the latter is less soluble than silver chloride, and, for this reason alone, iodine ions will replace chlorine or bromine ions in the case of the silver salts.

4. **Lead Salts** precipitate yellow lead iodide, soluble in considerable hot water and forming a colorless solution which deposits gold-yellow plates of PbI_2 on cooling.

5. **Palladous Chloride** (it is best to use sodium palladous chloride) precipitates black palladous iodide from dilute solutions of an iodide (difference from chlorine and bromine),

$$Na_2[PdCl_4] + 2\,KI = 2\,NaCl + 2\,KCl + \mathbf{PdI_2},$$

which is readily soluble in an excess of potassium iodide.

6. **Cupric Salts** are reduced by iodides, causing the separation of a brownish mixture of cuprous iodide and iodine:

$$2\,Cu^{++} + 4\,I^- \rightarrow \mathbf{Cu_2I_2} + I_2.$$

If sulfurous acid, sodium thiosulfate or ferrous sulfate is then added to the solution, a nearly white deposit of cuprous iodide is obtained, owing to the free iodine being changed to hydriodic acid by the reducing agent:

$$SO_3^{--} + H_2O + I_2 \rightarrow SO_4^{--} + 2\,H^+ + 2\,I^-;$$
$$2\,S_2O_3^{--} + I_2 \rightarrow S_4O_6^{--} + 2\,I^-.$$

7. **Nitrous Acid.** — If a dilute solution of an iodide is treated with nitrous acid, iodine separates out and the solution becomes yellow or brown in color (difference from chlorides and bromides):

$$2\,HNO_2 + 2\,HI = 2\,NO + I_2 + 2\,H_2O.$$

This extremely sensitive reaction is best performed as follows:

Prepare a solution of nitrous acid in concentrated sulfuric acid by heating arsenic trioxide with nitric acid (sp. gr. 1.30-1.35) and conducting the gases evolved (NO_2 and NO) into sulfuric acid (sp. gr. 1.75-1.80):

$$As_2O_3 + 2\,HNO_3 = As_2O_5 + H_2O + NO_2\uparrow + NO\uparrow,$$
$$2\,SO_2\begin{matrix}\diagup OH\\ \diagdown OH\end{matrix} + NO_2 + NO = H_2O + 2\,SO_2\begin{matrix}\diagup OH\\ \diagdown O(NO).\end{matrix}$$

This solution of nitrosyl sulfuric acid is sometimes called "nitrose." It can be kept for some time, but water decomposes it into nitrous and sulfuric acids:

$$SO_2\begin{matrix}\diagup OH\\ \diagdown ONO\end{matrix} + HOH = H_2SO_4 + HNO_2.$$

Treat the solution to be tested with a few drops of *nitrose* and shake with a little carbon disulfide or chloroform; if an iodide is present, iodine is liberated, which colors the carbon disulfide or chloroform.

8. **Potassium Dichromate,** in the presence of dilute sulfuric acid, causes the separation of iodine from dilute iodide solutions in the cold; the iodine can be more easily recognized by shaking the solution with chloroform or carbon disulfide (difference from bromine):

$$Cr_2O_7^{--} + 6\,I^- + 14\,H^+ \rightarrow 2\,Cr^{+++} + 7\,H_2O + 3\,I_2.$$

By heating a mixture of solid iodide and solid potassium dichromate with concentrated sulfuric acid, iodine is set free (according

to the above equation), which distills over, and can be condensed in the receiver. No chromium is carried over by this reaction (difference from chlorine).

9. **Potassium Permanganate** oxidizes hydriodic acid more readily than it acts upon hydrobromic or hydrochloric acids. The oxidation will take place in dilute acetic acid solutions containing considerable sodium acetate.

10. **Mercuric Chloride** produces scarlet mercuric iodide, soluble in an excess of potassium iodide:

$$Hg^{++} + 2\,I^- \rightarrow HgI_2,$$
$$HgI_2 + 2\,I^- \rightarrow [HgI_4]^{--}.$$

If a solution of an alkali iodide is treated with ammonia and a little potassium hydroxide and then with a few drops of mercuric chloride, a reddish-brown precipitate of dimercuric-ammonium iodide is obtained. This is a sensitive reaction.

11. **Chlorine Water** sets free iodine from iodides,

$$2\,KI + Cl_2 = 2\,KCl + I_2,$$

which colors carbon disulfide reddish-violet, or starch-paste blue.

By adding an excess of chlorine water, the violet color disappears. the iodine being oxidized to colorless iodic acid:

$$I_2 + 6\,H_2O + 5\,Cl_2 = 10\,HCl + 2\,HIO_3.$$

Detection of Iodine in Non-electrolytes

The processes to be employed are the same as those described for detecting chlorine in non-electrolytes (see p. 311).

FREE IODINE

Free iodine forms scales resembling graphite in appearance; its sp. gr. is 4.94 at 17°. It melts at 114° (at the same temperature as sulfur), but begins to volatilize at ordinary temperatures, and is completely transformed into violet vapors at 200°.

Iodine is only slightly soluble in water (100 parts of water dissolve 0.02 part of iodine) but is soluble to a considerable extent in alcohol and ether, forming brown solutions, and it is much more soluble in carbon disulfide, carbon tetrachloride and in chloroform; practically all the iodine can be removed from an aqueous solution by shaking a few times with either of these solvents (cf. p. 17). Iodine is very soluble in hydriodic acid, or in a solution of an alkali iodide, forming triiodide ions:

$$I^- + I_2 \rightleftarrows I_3^-.$$

The solution of the triiodide shows all the reactions of free iodine, but the vapor tension of the iodine is much less than in a solution of pure water because only a little free iodine is actually present at any one time.

Commercial iodine always contains water, chlorine, bromine, and often cyanogen (iodine cyanide) as impurities.

An aqueous solution of iodine is a weak oxidizing agent. If hydrogen sulfide is passed through an aqueous solution of iodine, it becomes colorless and turbid, owing to the separation of sulfur:

$$H_2S + I_2 = 2\,HI + S.$$

Solid iodine is not acted upon at ordinary temperatures by hydrogen sulfide; heat is necessary to produce the endothermic hydriodic acid.

In aqueous solution the necessary heat energy is furnished by the solution of the hydriodic acid formed in water. The fact that solid iodine is not acted upon by hydrogen sulfide, while it decomposes arsine, is utilized in the preparation of hydrogen sulfide containing no arsenic from pyrites containing arsenic (cf. p. 249). The mixture of hydrogen sulfide and arsine is passed over iodine, and the latter only is removed.

Sodium Thiosulfate decolorizes iodine solutions, forming sodium tetrathionate and sodium iodide:

$$2\,S_2O_3^{--} + I_2 \rightarrow S_4O_6^{--} + 2\,I^-.$$

Chlorine and bromine react in exactly the same way upon sodium thiosulfate solutions when they are not present in excess. In the latter case the reaction goes further and the tetrathionate is oxidized to sulfate and sulfuric acid with deposition of sulfur, and the sulfur itself is gradually oxidized to sulfuric acid by the halogens:

$$2\,S_4O_6^{--} + 12\,H_2O + 8\,Cl_2 \rightarrow 16\,Cl^- + 6\,SO_4^{--} + 24\,H^+ + 2\,S,$$
$$2\,S + 8\,H_2O + 6\,Cl_2 \rightarrow 16\,H^+ + 2\,SO_4^{--} + 12\,Cl^-.$$

Other weak oxidizing agents, such as ferric and cupric salts, act upon thiosulfate similar to iodine (see Thiosulfuric acid).

Starch Paste. — Free iodine colors starch paste blue, but only in the presence of hydriodic acid or a soluble iodide.

Opinions differ concerning the composition of the blue "iodide of starch." Some hold that it is a compound, while others regard it as a solid solution.* According to Mylius,† iodide of starch is the hydriodic acid compound of an iodine addition-product of starch, containing about 18 per cent iodine, corresponding to the formula $[C_{24}H_{40}O_{20}I]_4 \cdot HI$. This compound acts as an acid. If iodide of starch is produced

* Küster, *Ann.*, **283**, 689 (1894), C. O. Harz, *Chem. Zentr.*, **1898**, I, 1018; Andrews and Götsch, *J. Am. Chem. Soc.*, **24**, 865 (1906); Padra and Savori, *Chem. Zentrabl.*, **1905**, I, 1593; Katyama, *Z. anorg. Chem.*, **56**, 209 (1907).

† Mylius, *Ber.*, **20**, 688, and C. Lonnes, *Z. anal. Chem.*, **33**, 409.

in a neutral solution, in the presence of iodides, a salt of the above acid is formed, of which Mylius isolated the barium salt. Iodide of starch, then, can be regarded as a double salt, similar to carnallite, $MgCl_2 \cdot KCl \cdot 6\,H_2O$. In dilute solutions it must be dissociated into its components, e.g., the potassium salt

$$[C_{24}H_{40}O_{20}I]_4 \cdot KI \rightleftarrows 4\,[C_{24}H_{40}O_{20}I] + KI,$$

and if we assume that the compound $C_{24}H_{40}O_{20}I$ is colorless, the aqueous solution of starch iodide will be colorless; but on increasing the concentration of the alkali iodide, the double salt will be less dissociated and the blue color of the undissociated compound will appear, which corresponds with the facts. If a dilute aqueous iodine solution (obtained by shaking iodine with water) is added drop by drop to a dilute aqueous starch solution, a blue color will appear at the spot where the two solutions first come in contact, but this color will disappear on stirring. If some potassium (or other) iodide is added to the colorless solution of the starch and iodine, a permanent blue coloration will at once appear.*

The temporary appearance of the blue color, immediately on adding the iodine solution, is probably due to the fact that the iodine first forms a substitution product with the starch, setting free hydriodic acid, which furnishes the conditions for the formation of the iodide of starch.

The fact that a starch solution containing an iodide is much more sensitive than one in pure water has been known for a long time.

Detection of Hydrochloric, Hydrobromic, and Hydriodic Acids in the Presence of One Another

METHOD A

The solution to be tested should contain the alkali salts of the above acids. Half of this solution is taken for the bromide and iodide test, while the other half is retained for the chloride test.

(*a*) *Detection of Bromine and Iodine*

1. Acidify the solution with dilute sulfuric acid, add a little carbon disulfide, or chloroform, a drop of chlorine water and shake. If *iodine* is present (even in the presence of bromine), the carbon disulfide will be colored reddish-violet.

To detect *bromine* shake repeatedly after the addition of small portions of chlorine water, until the reddish-violet color has disappeared, showing that the iodine has been completely oxidized to iodic acid; the brown color of the bromine dissolved in the carbon disulfide will then appear and become a pale yellow on further addition of chlorine water.

2. Instead of using chlorine water, it is often better to test for iodine (especially when only small amounts are present, as in mineral waters) with nitrous acid. Slightly acidify the solution to be tested for iodine and bromine with dilute sulfuric acid, add carbon disulfide and a few drops of a solution of nitrous acid in sulfuric acid and shake the mixture. If the carbon disulfide is colored reddish-violet, iodine is present. Pour off the aqueous solution (through a moistened filter, in order to remove any suspended drops of colored carbon disulfide), add chlorine water and shake the solution with fresh carbon disulfide. If the latter now assumes a brown color, bromine is present.

* The blue color disappears on heating the solution, but reappears on cooling.

(b) *Detection of Chlorine*

The simplest way of separating chlorine from bromine and iodine is by fractional precipitation with silver nitrate. If the solution containing salts of the three halogens is treated with dilute silver nitrate, drop by drop, the iodine will be first precipitated as yellow silver iodide, then the bromide as a pale yellow silver salt, and finally the chlorine as pure white silver chloride. To separate the chlorine from the other two halogens, acidify a little of the solution to be tested with nitric acid, add a drop of dilute silver nitrate solution (1 : 100) shake and boil the mixture, which causes the precipitate to collect together. If bromine or iodine is present, the precipitate is yellow. Filter off the precipitate and again treat with the dilute silver nitrate, etc., until a pure white precipitate of silver chloride is obtained, in case chlorine is present.

By filtering off the precipitate it is easy to tell whether it is pure white, for the slightest tinge of yellow will show against the white paper.

METHOD B

This method of analysis is based upon the different degrees of readiness with which the iodide, bromide and chloride ions are oxidized by 1 per cent potassium permanganate solution. In a dilute solution containing a little acetic acid and considerable sodium acetate, an iodide is immediately oxidized with liberation of iodine, which can be removed from the solution by shaking with a solvent which is immiscible with water (cf. p. 17). Under these conditions an appreciable quantity of bromide or chloride ions is not oxidized in the time required for the necessary operations with an iodide. When the concentration of the hydrogen ions is increased, by the addition of a prescribed quantity of sulfuric acid, the bromide is oxidized very rapidly while the rate of the corresponding reaction with chloride ions is so slow that scarcely any free chlorine is formed. The solution may even be boiled without losing more than a small fraction of the chloride ions originally present.

The increase in the oxidizing power of the permanganate upon the addition of hydrogen ions is a direct fulfillment of the mass-action principle (p. 13). In the reaction between permanganate and halogen ions, hydrogen ions are required,

$$2\,MnO_4^- + 6\,I^- + 8\,H^+ \rightarrow 2\,MnO_2 + 4\,H_2O + 3\,I_2,$$

or

$$2\,MnO_4^- + 10\,I^- + 16\,H^+ \rightarrow 2\,Mn^{++} + 8\,H_2O + 5\,I_2.$$

The permanganate will be reduced only to the quadrivalent condition, and manganese dioxide will be precipitated, when the supply of hydrogen ions is limited, but bivalent manganous cations will be formed to a greater extent when more acid is present.

In carrying out this method of analysis, it is very important that the directions should be closely followed as regards the quantities of acid added.

Procedure. — If the solution to be tested is acid, add sodium carbonate solution drop by drop until the solution no longer gives a decided red color to blue litmus paper. If too much sodium carbonate is added accidentally, add dilute nitric acid, drop by drop, until a very faint acid test is obtained in the well-stirred liquid. Then add 8 cc. of normal sodium acetate solution, 2 cc. of 6-normal acetic acid, and filter if any precipitate is formed. Add 3 cc. of chloroform and 1 per cent permanganate solution, 1 cc. at a time, until the aqueous solution after being vigorously shaken shows the pink color of permanganate. If an iodide is present, the chloroform will now be colored purple by the presence of free iodine.

Pour the mixture through a moistened filter to remove the chloroform and precipitated manganese dioxide; the wetting with water serves to prevent chloroform passing through the pores of the paper. Shake the filtrate, if necessary, with fresh portions of chloroform to extract all of the iodine from the aqueous solution (cf. p. 17), filtering through a fresh filter each time.

When all the iodine has been removed, transfer the solution to a separatory funnel, add 3 cc. of fresh chloroform, 5 cc. of 6-normal sulfuric acid and 1 cc. of the dilute permanganate, unless an excess of the last mentioned reagent is already present. Shake vigorously and then allow the chloroform to separate out beneath the water. If bromine is present, the chloroform will be colored yellow or orange.

Carefully remove the chloroform with the aid of the separatory funnel and transfer the aqueous solution to a porcelain dish. Add from 5 to 20 cc. of dilute permanganate, according to the amount of bromide probably present, and boil the mixture about five minutes, or until the volume of the solution has been reduced to 10 cc. Filter off the manganese dioxide precipitate; and, if the solution is still pink, add sulfurous acid drop by drop until it is colorless. Boiling the solution serves to oxidize the last traces of bromine ions present without oxidizing chlorine ions to any extent. The excess of permanganate reacts with manganous ions (formed by reduction of the permanganate) to form manganese dioxide,

$$2\,MnO_4^- + 3\,Mn^{++} + 2\,H_2O \rightarrow 5\,MnO_2 + 4\,H^+,$$

but the presence of hydrogen ions interferes with this reaction, in accordance with the mass-action law. Consequently, either owing to the fact that there is a deficiency of manganous ions in the solution or because the concentration of the hydrogen ions is too great, it is often necessary to add sulfurous acid to reduce the last traces of permanganate ion.

$$2\,MnO_4^- + 5\,SO_3^{--} + 6\,H^+ \rightarrow 2\,Mn^{++} + 5\,SO_4^{--} + 3\,H_2O.$$

Dilute the solution to 100 cc., filter if necessary, add 20 cc. of 6-normal nitric acid and a little silver nitrate solution. A curdy precipitate of silver chloride is formed if a chloride is present.

Remark. - The above method of separation is capable of giving excellent results. A solid substance can be tested for chloride, bromide and iodide after first heating it with phosphoric acid and collecting the distillate. If about 2 gms. of solid, 25 cc. of water and 10 cc. of 85 per cent phosphoric acid are used, all the iodine, bromine and chlorine will pass into the distillate. If any oxidizing agent is present, however, free iodine, free bromine and free chlorine will be formed in the order named. The free halogen can be removed by shaking the distillate with chloroform (cf. p. 326). If free chlorine is formed, it will dissolve in the chloroform. Iodine and bromine are recognized by the color they impart to the chloroform and liberate iodine from potassium iodide. After the removal of the free halogen, the distillate may be tested for hydriodic, hydrobromic and hydrochloric acids as described above. By distilling with phosphoric acid, halogen is obtained even from chlorates and bromates if a reducing agent is present.

Detection of Halogen in the Presence of Cyanide

Conduct carbon dioxide through the slightly alkaline solution until the escaping gas no longer gives any turbidity when passed into a nitric acid solution of silver nitrate.

The carbon dioxide may be prepared in a Kipp generator from marble and dilute hydrochloric acid and washed with sodium bicarbonate solution. The carbonic

acid expels the weaker hydrocyanic acid from its salts (cf. p. 10). Owing to the very poisonous nature of hydrocyanic acid, the expulsion of the gas should take place under a good hood.

After the removal of the hydrocyanic acid, test the solution in the usual way for halogens.

HYDROCYANIC ACID (PRUSSIC ACID), HCN

Occurrence. — The compound of hydrogen with the univalent cyanogen radical, CN, occurs to some extent in nature. It is found in all parts of a tree growing in Java (*Pangium Edule*), particularly in the seed kernels. Its compounds are found in many plants as a glucoside (amygdalin), which yields, on hydrolysis, a carbohydrate, benzaldehyde, and prussic acid:

$$\underset{\text{Amygdalin}}{C_{20}H_{27}NO_{11}} + 2\,H_2O = 2\,C_6H_{12}O_6 + \underset{\text{Benzaldehyde}}{C_6H_5CHO} + HCN.$$

This amygdalin is found in bitter almonds, in the fruit kernels of cherries, apricots, peaches, etc., and in the leaves of the common laurel tree (*Prunus Laurocerasus*).

Amygdalin is usually accompanied by a ferment, so that, on macerating the parts of the plant which contain the amygdalin, an aqueous solution of prussic acid is obtained (bitter-almond water).

Preparation. — If ammonia is passed over glowing carbon, ammonium cyanide is formed; so that this salt, as well as other cyanogen compounds, is found in the "gas-water" obtained by the dry distillation of coal.

Hydrocyanic acid may also be prepared by adding acid to many cyanogen compounds. If yellow prussiate of potash is treated with dilute sulfuric acid and distilled, prussic acid is evolved, which, after standing over solid calcium chloride, may be obtained in the anhydrous condition as a colorless, exceedingly poisonous liquid, smelling of bitter almonds, and boiling at 26.5° C.:

$$2\,K_4[Fe(CN)_6] + 6\,H_2SO_4 \rightarrow 6\,KHSO_4 + K_2Fe[Fe(CN)_6] + 6\,HCN.$$

The most convenient method for preparing anhydrous hydrogen cyanide* consists in allowing a mixture of equal volumes sulfuric acid and water to drop upon sticks of 98 per cent potassium cyanide. Hydrogen cyanide is evolved, contaminated with traces of water which can be removed by allowing the liquid to stand over solid calcium chloride.

Properties. — Hydrocyanic acid gas burns with a reddish flame, and mixes in all proportions with water, alcohol, and ether.

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* J. WADE and L. PANTING, *Proc. Chem. Soc.*, **190**, 49 (1897–8).

Aqueous hydrocyanic acid cannot be kept indefinitely; a brown deposit soon appears, and ammonium formate is formed:

$$HCN + 2\,HOH = HCO_2NH_4.$$

If a little mineral acid is added to the aqueous solution, it may be kept much longer; but, even then, ammonia and formic acid will be formed after a long time. Cold concentrated hydrochloric acid converts hydrocyanic acid into formamide, $HCN + H_2O = HCONH_2$, but on warming this compound is decomposed into carbon monoxide and ammonia.

Hydrocyanic acid in aqueous solution is a very poor conductor of electricity; in other words, it is a very weak acid, and is ionized only to a slight extent. The ionization constant is 4.7×10^{-10} at 18°. In 0.1-normal solution it is only 0.006 of 1 per cent ionized.

The salts of hydrocyanic acid, the cyanides, are very similar in their properties to the corresponding halogen compounds, but are distinguished by their ability to form stable complex salts, which contain scarcely any cyanogen ions in aqueous solution, and consequently do not give some of the reactions for hydrocyanic acid.

Solubility of Cyanides. — The cyanides of the alkalies and alkaline earths are readily soluble in water, but hydrolysis (p. 49) takes place to a considerable extent:

$$CN^- + H_2O \rightarrow OH^- + HCN.$$

Since hydrocyanic acid is only slightly ionized, the aqueous solution of an alkali cyanide behaves like a solution of alkali hydroxide containing free prussic acid; the odor of the latter can be easily detected. The salts of hydrocyanic acid are decomposed by acids, even by weak carbonic acid.

The remaining cyanides, with the exception of mercuric cyanide, are insoluble in water.

Reactions in the Wet Way

1. **Dilute Sulfuric Acid** decomposes solutions of all soluble cyanides, with the exception of mercuric cyanide, setting free hydrocyanic acid in the cold (recognizable by its odor). Danger!

The insoluble cyanides are decomposed by dilute sulfuric acid only on warming.

2. **Concentrated Sulfuric Acid** decomposes all cyanides on warming, the complex cyanides as well as the simple ones. The metals are then obtained in the form of acid sulfates, the carbon of the

cyanogen is changed to carbon monoxide, and the nitrogen into ammonium sulfate:

$$Ni(CN)_2 + 2\,H_2SO_4 + 2\,H_2O = NiSO_4 + (NH_4)_2SO_4 + 2\,CO\uparrow.$$

With mercuric cyanide, besides carbon monoxide, sulfur dioxide and carbon dioxide are obtained; for mercuric cyanide is decomposed at the temperature of boiling sulfuric acid into mercury and cyanogen and the former dissolves in the hot sulfuric acid, with formation of mercuric sulfate and evolution of sulfur dioxide:

$$Hg(CN)_2 + 6\,H_2SO_4 \rightarrow 2\,NH_4HSO_4 + Hg(HSO_4)_2 + CO\uparrow + CO_2\uparrow + SO_2\uparrow + SO_3\uparrow.$$

3. **Silver Nitrate.** — If silver nitrate is added to a solution of an alkali cyanide drop by drop, a precipitate is formed on the addition of each drop, which, however, redissolves on stirring the liquid, for silver cyanide is soluble in an excess of alkali cyanide:

$$CN^- + Ag^+ \rightarrow \mathbf{AgCN};$$
$$\mathbf{AgCN} + CN^- \rightarrow [Ag(CN)_2]^-.$$

The complex silver cyanide ion is decomposed by further addition of silver nitrate, being finally completely transformed into insoluble silver cyanide:

$$[Ag(CN)_2]^- + Ag^+ \rightarrow 2\,\mathbf{AgCN}.$$

Consequently the precipitation is complete only when an excess of silver nitrate is added.

Silver cyanide is insoluble in water and dilute nitric acid, perceptibly soluble in concentrated nitric acid, and readily soluble in ammonia, sodium thiosulfate, and potassium cyanide solutions. Dilute nitric acid reprecipitates silver cyanide from the solution in ammonia or potassium cyanide.

Concentrated hydrochloric acid decomposes silver cyanide, on warming, into silver chloride, with evolution of hydrocyanic acid (difference from silver chloride, bromide, or iodide).

By igniting silver cyanide, there is formed cyanogen gas, metallic silver, and brown, difficultly-volatile paracyanogen, which, on further heating, is completely volatilized, leaving behind pure silver:

$$2\,\mathbf{AgCN} = 2\,\mathbf{Ag} + (CN)_2\uparrow$$

Much more certain than the silver nitrate test are the tests for hydrocyanic acid which depend upon the formation of Prussian blue or of ferric thiocyanate.

4. **Prussian Blue Reaction.** — Prussian blue is formed by the action of ferric salts upon potassium ferrocyanide (cf. p. 159).

$$3\,[Fe(CN)_6]^{----} + 4\,Fe^{+++} \rightarrow \mathbf{Fe_4[Fe(CN)_6]_3}.$$

In order, therefore, to apply this reaction to potassium cyanide, etc., it is necessary first to transform the cyanide into potassium ferrocyanide. This may be accomplished by the addition of a ferrous salt, whereby ferrous cyanide is first formed, which dissolves in an excess of potassium cyanide, forming potassium ferrocyanide:

$$(a)\ Fe^{++} + 2\,CN^- \rightarrow \mathbf{Fe(CN)_2};$$

$$(b)\ \mathbf{Fe(CN)_2} + 4\,CN^- \rightarrow [Fe(CN)_6]^{=\!=}.$$

Potassium ferrocyanide is formed even more readily by the action of potassium cyanide upon ferrous hydroxide:

$$\mathbf{Fe(OH)_2} + 2\,CN^- \rightarrow \mathbf{Fe(CN)_2} + 2\,OH^-;$$

$$\mathbf{Fe(CN)_2} + 4\,CN^- \rightarrow [Fe(CN)_6]^{=\!=}.$$

For the formation of the potassium ferrocyanide a little iron and considerable potassium cyanide are required. Consequently, to bring about the reaction, add a little ferrous sulfate to the alkaline solution of an alkali cyanide and boil the mixture. Then add a little hydrochloric acid, whereby a clear solution is obtained, which gives, with a little ferric chloride, the blue precipitate. If only traces of hydrocyanic acid are present, the solution appears green at first, but, after standing some time, "flocks" of Prussian blue will be precipitated.

The Prussian blue reaction is used for the detection of nitrogen in organic substances (cf. p. 336).

Remark. — When only a trace of cyanide is present, the Prussian blue seen through yellow ferric chloride appears green. If the ferric chloride solution is diluted largely to get rid of the yellow color, the iron is then largely in colloidal solution, as a result of the formation of basic salt by hydrolysis; such a solution reacts very slowly with ferrocyanide. A more sensitive test for *traces* of ferrocyanide is obtained by adding a saturated solution of *ferrous* sulfate. Such a solution always contains enough ferric ions to give the Prussian blue test with a trace of ferrocyanide ions. When more than a trace of ferrocyanide is present, however, it is best to test with ferric chloride solution as outlined above.

5. **The Ferric Thiocyanate Reaction.** — Potassium thiocyanate produces a red coloration with a ferric salt, owing to the formation of slightly ionized ferric thiocyanate (cf. p. 158):

$$3\,CNS^- + Fe^{+++} \rightarrow Fe(CNS)_3,$$

The cyanide, therefore, must be changed to thiocyanate in order to apply this reaction, which can be done by heating with sulfur,

$$KCN + S = KCNS,$$

or, better, by treatment with an alkaline polysulfide,

$$KCN + (NH_4)_2S_2 = (NH_4)_2S + KCNS.$$

To the concentrated solution of the cyanide (in a porcelain dish) add a little yellow ammonium sulfide and evaporate the mixture to dryness on the water-bath. Add a little hydrochloric acid and a drop of ferric chloride solution; the characteristic blood-red coloration will be produced if only traces of cyanide are present.

It is necessary to acidify in order to destroy the $(NH_4)_2S$, which would precipitate black Fe_2S_3 with $FeCl_3$ and the red coloration would not appear.

6. **Mercurous Nitrate** produces a gray precipitate of metallic mercury when added to a solution of an alkali cyanide (difference from a chloride, bromide, or iodide):

$$Hg_2^{++} + 2\,CN^- \rightarrow Hg(CN)_2 + \mathbf{Hg}.$$

7. **Sodium Nitroprusside Reaction.** — If a solution of hydrocyanic acid or of an alkali cyanide is treated with a few drops of alkali nitrite solution and then with two or three drops of ferric chloride and just enough very dilute sulfuric acid to change the color of the ferric salt that forms from brown to light yellow, then upon heating to the boiling point, cooling and adding enough ammonia to precipitate the excess of ferric ion, a filtrate is obtained which will give a violet coloration with a few drops of hydrogen sulfide water. The reaction depends upon the formation of the nitroprusside ion $[Fe(CN)_5NO]^{--}$ which gives a reddish-violet color with sulfide ions.

8. **Blue Starch-Iodide Solution** is decolorized by a trace of alkali cyanide and a little sulfuric acid: the iodine unites with the hydrocyanic acid to form cyanogen iodide and hydriodic acid,

$$HCN + I_2 \rightarrow CNI + HI.$$

The reaction is very sensitive but many other substances decolorize blue iodide of starch.

Behavior of Mercuric Cyanide

Mercuric cyanide, $Hg(CN)_2$, is a non-electrolyte, is quite soluble in water, alcohol and ether, and behaves quite differently from all other cyanides. All the above-mentioned reactions, with the exception of the ferric thiocyanate test, fail with this compound. Mercuric cyanide solution gives no precipitate with silver nitrate, but a readily soluble double salt is formed,

$$Hg(CN)_2 \cdot AgNO_3 \cdot 2\,H_2O.$$

Similarly there is no precipitate formed with ammonia, potassium iodide, alkali hydroxide, or alkali carbonate because all these reagents give, under ordinary conditions, precipitates of mercuric compounds which are soluble in potassium cyanide. Thus, for example, mercuric oxide dissolves easily in potassium cyanide:

$$\mathbf{HgO} + 2\,KCN + H_2O = 2\,KOH + Hg(CN)_2.$$

Mercuric oxide itself is fairly soluble in mercuric cyanide:

$$\mathbf{HgO} + Hg(CN)_2 = O\begin{matrix}\diagup Hg-CN \\ \diagdown Hg-CN\end{matrix}.$$

Hydrochloric, hydrobromic and hydriodic acid decompose mercuric cyanide readily, but dilute sulfuric acid alone has little action upon it. In the presence of a soluble chloride, however, mercuric cyanide is decomposed easily by sulfuric acid, or even by oxalic acid or tartaric acid. If, therefore, a solution of mercuric cyanide is treated with common salt and dilute sulfuric, oxalic or tartaric acid, then, on subjecting the mixture to distillation, a distillate is obtained containing hydrocyanic acid, and gives all the tests characteristic of this acid.

Mercuric cyanide in solution is acted upon by hydrogen sulfide or by alkali sulfides, forming mercuric sulfide and hydrocyanic acid, or one of its salts. If the black precipitate is removed by filtration, the ferric thiocyanate reaction is obtained without difficulty.

$$Hg(CN)_2 + H_2S \rightarrow HgS + 2\,HCN.$$

Behavior of Cyanides on Ignition

The cyanides of the alkalies and alkaline earths fuse without decomposition when heated out of contact with the air; heated in contact with air, they absorb oxygen with avidity, forming cyanates:

$$2\,KCN + O_2 = 2\,KCNO.$$

Consequently the alkali cyanides are strong reducing agents (cf. p. 277).

The cyanides of the bivalent heavy metals are decomposed on ignition, out of contact with the air, into nitrogen and metallic carbide; the latter often being further decomposed into metal and carbon:

$$3\,Fe(CN)_2 = Fe_3C + C + 2\,(CN)_2\uparrow + N_2\uparrow,$$
$$Pb(CN)_2 = Pb + 2\,C + N_2\uparrow.$$

The cyanides of the trivalent metals are unknown in the free state; those of the noble metals are decomposed, by igniting, into metal and dicyanogen:

$$2\,AgCN = 2\,Ag + (CN)_2\uparrow,$$
$$Hg(CN)_2 = Hg + (CN)_2\uparrow.$$

It is a characteristic property of the cyanides of the heavy metals that they are readily soluble in alkali cyanide solutions, forming very stable complex compounds, which are to be regarded as salts of the following acids:

$$H[R^{I}(CN)_2],\quad H_2[R^{II}(CN)_4],\quad H_3[R^{III}(CN)_6]\quad \text{and}\quad H_4[R^{II}(CN)_6].$$

The first two of the above acids are so unstable that they are decomposed, as soon as they are set free, into hydrocyanic acid and cyanide:

$$H[R(CN)_2] = HCN + RCN;$$
$$H_2[R(CN)_4] = 2\,HCN + R(CN)_2.$$

Consequently all cyanides which are derived from these acids evolve hydrocyanic acid when treated with dilute hydrochloric or sulfuric acid in the cold. Such compounds are:

$$K[Ag(CN)]_2,\ K[Au(CN)]_2,\ K_2[Ni(CN)_4],\ K_2[Zn(CN)_4],\ K_2[Cd(CN)_4],\ \text{etc.}$$

These salts must be regarded as complex compounds (p. 24), for their aqueous solutions contain almost no heavy metal ions; they are not precipitated by caustic alkali, alkali carbonate, or ammonia. From this fact it follows that the oxides of these metals are soluble in cyanides of the alkalies, forming the following complex salts:

$$Ag_2O + 4\,CN^- + H_2O \rightarrow 2\,OH^- + 2\,[Ag(CN)_2]^-;$$
$$NiO + 4\,CN^- + H_2O \rightarrow 2\,OH^- + [Ni(CN)_4]^{--};$$
$$ZnO + 4\,CN^- + H_2O \rightarrow 2\,OH^- + [Zn(CN)_4]^{--};$$
$$CdO + 4\,CN^- + H_2O \rightarrow 2\,OH^- + [Cd(CN)_4]^{--}.$$

Hydrogen sulfide decomposes the silver and cadmium salts without difficulty, the zinc salt slightly, and the nickel salt not at all.

The acids of the general formula $H_3[R^{III}(CN)_6]$ and $H_4[R^{II}(CN)_6]$ are, in contrast with the above acids, quite stable in the free state, and can be usually obtained, without the loss of hydrocyanic acid, by acidifying a solution of one of their salts with cold dilute mineral acid; but, on warming the acid solution, hydrocyanic acid is given off.

As typical representatives of these acids we have ferrocyanic, ferricyanic and cobalticyanic acids.*

Ferrocyanic and ferricyanic acids will be discussed separately; but before doing so a brief description will be given of

DICYANOGEN

This compound is obtained by heating the cyanides of the noble metals, as a colorless gas with a disagreeable odor; it burns with a reddish flame, and is soluble in water (25 parts water dissolve 100 parts of dicyanogen). The aqueous solution cannot be kept very long, as brownish "flocks" separate out little by little (azulmic acid, $C_4H_5N_5O$) and the solution then contains ammonium cyanide, ammonium carbonate, ammonium oxalate, and urea.

Just as chlorine acts upon caustic alkalies, forming chloride and hypochlorite, so dicyanogen reacts with them, forming a cyanide and a cyanate:

$$Cl_2 + 2\,KOH = KCl + H_2O + KOCl;$$

$$(CN)_2 + 2\,KOH = KCN + H_2O + KOCN.$$

On conducting hydrogen sulfide into a solution of dicyanogen, a red, crystalline precipitate of hydrorubianic acid is obtained: $(CN)_2 + 2\,H_2S = (CSNH_2)_2$. Cf. p. 232.

Detection of Nitrogen in Organic Substances. (Lassaigne.)

If a little nitrogenous, organic substance is placed with some metallic sodium in a small glass tube which is closed at one end, and the tube is heated till the glass begins to soften, then the nitrogen and some of the carbon of the organic substance will combine with sodium to form sodium cyanide. After heating for two minutes, plunge the hot end of the glass tube in a little water, whereby the glass breaks and the contents of the tube are immediately wet by water. Filter off the alkaline solution containing the sodium cyanide from the residual carbon and glass splinters, add a little ferrous sulfate solution and boil. Finally add a few drops of ferric chloride solution and enough hydrochloric acid to neutralize the alkali. If nitrogen was present in the original substance, Prussian blue is now obtained.

Remark. — Certain nitrogenous substances are decomposed with evolution of nitrogen before the temperature required for the cyanide formation is reached,† and thus the nitrogen escapes the Lassaigne reaction; in other cases the experiment fails on account of the extreme volatility of the organic substance.‡

According to E. A. Kehrer,§ the Lassaigne reaction gives positive results in all cases if the sodium is first heated by itself and then brought in contact with the vapors of the organic material. The experiment is carried out in a small tube,

* Cobaltocyanic acid is extremely unstable, like mangano- and manganicyanic acids. Its salts evolve HCN when treated with cold, dilute, mineral acids.

† GRÄBE, *Ber.*, **17**, 1178 (1884).

‡ FEIST, *Ber.*, **35**, 1559 (1902).

§ *Ber.*, **35**, 2523 (1902).

drawn out at the closed end, such as used for the arsenic test (cf. Fig. 21, p. 250). Place the substance in the restricted part of the tube and then, in the wider part, just before the restriction is reached, introduce a small piece of sodium which has been rolled between the fingers and freed from petroleum by touching it to filter paper. Heat the sodium until it glows and then, by means of another small flame, heat the substance to be tested so that it melts and the vapors just rise up to the glowing sodium but hardly reach through it. By taking away the small flame, the vapors can be made to condense and be driven toward the glowing sodium again. Otherwise, carry out the test exactly as described above.

For the detection of *traces* of nitrogen it is best not to add any ferric chloride, but to add a saturated solution of ferrous sulfate, after adding the acid (cf. p. 333).

Detection of Hydrocyanic Acid in the Presence of Halogen Acid, Ferrocyanic, Ferricyanic and Thiocyanic Acids

Hydrocyanic acid is by far the weakest of all the above acids (cf. p. 10) and it alone is expelled from its salts by means of carbonic acid at the temperature of boiling water.

Place the solution to be tested in a small Erlenmeyer flask, add 0.6 to 1 gm. of $NaHCO_3$ and close the flask with a two-hole rubber stopper. Insert through one of the holes in the stopper a piece of glass tubing that reaches nearly to the bottom of the flask and serves for the introduction of the carbon dioxide gas; through the other hole insert a piece of tubing that reaches only to the bottom of the rubber stopper and serves for the escape of the gas. Pass carbon dioxide gas (cf. p. 328), through the liquid in the flask, gradually heat to boiling and conduct the escaping vapors into silver nitrate solution which has been acidified with nitric acid.

If cyanide is present in the original solution, a white precipitate of silver cyanide is formed in the silver nitrate solution within a short time. To confirm the test, decant off the solution from the precipitate and wash it a few times by decantation with water. Cover the precipitate with a little yellow ammonium sulfide, warm, and filter. Evaporate the filtrate to a small volume and treat with a little hydrochloric acid and a few drops of ferric chloride solution. A red color, due to ferric thiocyanate, proves the presence of cyanide.

FERROCYANIC ACID, $H_4[Fe(CN)_6]$

Ferrocyanic acid is a white, solid substance, which is readily soluble in water and in alcohol; the solution is strongly acid and soon becomes blue on exposure to air. The salts of this acid are much more stable than the acid itself, being all prepared from the potassium salt, the so-called *yellow prussiate of potash*. This potassium salt, the most important ferrocyanide of commerce, is obtained by the fusion of organic substances containing nitrogen and sulfur (blood, etc.) with potash and metallic iron, and by lixiviating the product of the fusion with water.

In the melt, iron sulfide and potassium cyanide are found, which, on treatment with water, are changed to potassium ferrocyanide and potassium sulfide,

$$FeS + 6\,KCN = K_4[Fe(CN)_6] + K_2S,$$

and, on evaporating the solution, the former salt separates out (with three molecules of water of crystallization) in the form of large, yellow, tetragonal octahedrons.

Recently this salt has been obtained as a by-product in the manufacture of illuminating-gas, Prussian blue and ammonium thiocyanate being formed during the purification of the gas.

The following equations will give some idea of the formation of potassium ferrocyanide in the gas-house:

1. $Fe_7(CN)_{18} + 6\,Ca(OH)_2 = 4\,\mathbf{Fe(OH)_3} + 3\,\mathbf{Ca_2[Fe(CN)_6]}$;
2. $\mathbf{Ca_2[Fe(CN)_6]} + 2\,KCl = \underset{\text{Very difficultly soluble}}{\mathbf{K_2Ca[Fe(CN)_6]}} + CaCl_2$;
3. $K_2Ca[Fe(CN)_6] + K_2CO_3 = \mathbf{CaCO_3} + K_4[Fe(CN)_6]$.

Solubility of Ferrocyanides. — The ferrocyanides of the alkalies and alkaline earths are soluble in water; but the remaining salts dissolve with difficulty (if at all) in water and in cold dilute acids.

Reactions in the Wet Way

1. **Dilute Sulfuric Acid.** — The ferrocyanides are not decomposed by cold sulfuric acid, but break up at the boiling temperature with evolution of hydrocyanic acid:

$$2\,K_4[Fe(CN)_6] + 6\,H_2SO_4 \rightarrow K_2Fe[Fe(CN)_6] + 6\,KHSO_4 + 6\,HCN\uparrow.$$

2. **Concentrated Sulfuric Acid** decomposes ferrocyanides completely, on warming, with evolution of carbon monoxide, which burns with a blue flame:

$$K_4[Fe(CN)_6]+11H_2SO_4+6H_2O=FeSO_4+4KHSO_4+6NH_4HSO_4+6CO\uparrow.$$

SO_3 is also liberated by this reaction, as a part of the ferrous sulfate is oxidized by the sulfuric acid to ferric sulfate:

$$2FeSO_4 + 2SO_3 \rightarrow Fe_2(SO_4)_3 + SO_2\uparrow.$$

3. **Silver Nitrate** produces a white precipitate of silver ferrocyanide

$$[Fe(CN)_6]^{=} + 4Ag^+ \rightarrow \mathbf{Ag_4[Fe(CN)_6]},$$

insoluble in dilute nitric acid and ammonia, but soluble in potassium cyanide solution. On treatment with concentrated nitric acid, it is changed to orange silver ferricyanide, and is then soluble in ammonia.

4. **Barium Chloride** gives no precipitation.

5. **Ferric Salts** produce a precipitate of Prussian blue in neutral or acid solutions (cf. p. 159).

6. **Ferrous Salts** yield a light blue precipitate, which changes to a darker blue on exposure to the air (cf. p. 155).

7. **Cupric and Uranyl Salts** produce brown precipitates.

To detect ferrocyanic acid in an insoluble ferrocyanide, boil the latter with caustic alkali solution; metallic hydroxide and a ferrocyanide will be formed. Thus, Prussian blue yields insoluble ferric hydroxide and a soluble ferrocyanide:

$$Fe_4[Fe(CN)_6]_3 + 12OH^- \rightarrow 4\mathbf{Fe(OH)_3} + 3[Fe(CN)_6]^{=}.$$

Filter off the insoluble hydroxide, add dilute hydrochloric acid to the filtrate and treat with ferric chloride. Prussian blue is again formed if a ferrocyanide is present.

Prussian blue is often used in wall-papers as a pigment. If it is desired to detect the presence of this compound in a wall-paper, cut about 100 sq. cm. of the paper into small pieces, boil them with caustic potash solution, filter, and treat the filtrate according to the method just described. In a few hours a distinct blue precipitate of Prussian blue will be visible in the bottom of the test-tube, if it was originally present.

Some insoluble ferrocyanides do not yield the hydroxide of the metal on treatment with caustic alkali. Thus the brown uranyl ferrocyanide yields insoluble yellow potassium uranate and soluble potassium ferrocyanide (cf. p. 164).

Insoluble zinc ferrocyanide is completely soluble in caustic alkali, forming an alkali zincate and soluble ferrocyanide:

$$\mathbf{Zn_2[Fe(CN)_6]} + 8OH^- \rightarrow [Fe(CN)_6]^{=} + 2ZnO_2^{=} + 4H_2O.$$

In order to separate the zinc from the ferrocyanide, pass carbon dioxide gas into the solution, boil, and filter off the insoluble zinc carbonate. The filtrate then contains potassium ferrocyanide, which can be detected as described above.

8. **Lead Salts** precipitate white lead ferrocyanide insoluble in dilute nitric acid.

9. ***Thorium Nitrate*** *added to a slightly acid solution of an alkali ferrocyanide produces a white precipitate, difficult to filter (difference from ferricyanic and thiocyanic acids).*

10. If a solution of potassium ferrocyanide, which is not too dilute, is treated with hydrochloric acid, the addition of ether causes the separation of solid ferricyanic acid at the zone of contact of the ether and aqueous solution.

11. Alkali ferrocyanides are *not* decomposed in cold, aqueous solutions by carbon dioxide but decomposition takes place if carbon dioxide is passed into a hot solution. Solutions of ferrocyanides made alkaline with sodium carbonate give no hydrocyanic acid when distilled in a stream of carbon dioxide; the same is true if sodium bicarbonate is used instead of sodium carbonate in this test.

Behavior of Ferrocyanides on Ignition

On being ignited, the ferrocyanides yield iron carbide, cyanide, cyanogen and nitrogen:

$$3\,K_4[Fe(CN)_6] = 12\,KCN + Fe_3C + C + 2\,(CN)_2\uparrow + N_2\uparrow$$

$$3\,Ag_4[Fe(CN)_6] = 12\,Ag + Fe_3C + C + 8\,(CN)_2\uparrow + N_2\uparrow .$$

FERRICYANIC ACID, $H_3[Fe(CN)_6]$

Ferricyanic acid forms brown needles, readily soluble in water. Its salts, the ferricyanides, are very stable, and are obtained by *oxidation* of the corresponding ferrocyanides. The most important of all these salts, potassium ferricyanide (red prussiate of potash), $K_3[Fe(CN)_6]$, is obtained by the oxidation of potassium ferrocyanide with chlorine:

$$2\,K_4[Fe(CN)_6] + Cl_2 = 2\,KCl + 2\,K_3[Fe(CN)_6].$$

Bromine, hydrogen peroxide, etc., may be used instead of chlorine.

Solubility of Ferricyanides. — The ferricyanides of the alkalies and alkaline earths, and the ferric salt of ferricyanic acid, are soluble in water, but the remaining salts are insoluble even in dilute acids.

Reactions in the Wet Way

1. **Dilute Sulfuric Acid** evolves no hydrocyanic acid in the cold (difference from cyanides), but does so on warming with the acid.

2. **Concentrated Sulfuric Acid** decomposes all ferricyanides, on warming, with the formation of sulfates and carbon monoxide:

$$K_3[Fe(CN)_6] + 11\,H_2SO_4 + 6\,H_2O =$$
$$= FeH(SO_4)_2 + 3\,KHSO_4 + 6\,NH_4HSO_4 + 6\,CO\uparrow.$$

3. **Silver Nitrate** produces orange silver ferricyanide:

$$[Fe(CN)_6]^{---} + 3\,Ag^{+} \rightarrow \mathbf{Ag_3[Fe(CN)_6]},$$

soluble in ammonia, but insoluble in nitric acid.

4. **Barium Chloride** gives no precipitation.

5. **Ferrous Salts** produce, in neutral and acid solutions, a precipitate of Turnbull's blue (cf. p. 155).

6. **Ferric Salts** produce no precipitation, but a brown coloration.

7. **Cupric Salts** yield green cupric ferricyanide:

$$2\,[Fe(CN)_6]^{---} + 3\,Cu^{++} \rightarrow \mathbf{Cu_3[Fe(CN)_6]_2}.$$

8. **Behavior of Ferricyanides in Alkaline Solutions.** — Ferricyanic acid is a strong oxidizing agent in alkaline solutions, being readily reduced to ferrocyanic acid by sulfide, iodide, sulfite, ferrous hydroxide, manganous hydroxide, lead oxide, hydrogen peroxide, starch, cellulose (paper), etc.; e.g.:

$$2\,[Fe(CN)_6]^{---} + S^{--} \rightarrow 2\,[Fe(CN)_6]^{--} + \mathbf{S};$$
$$2\,[Fe(CN)_6]^{---} + 2\,I^- \rightarrow 2\,[Fe(CN)_6]^{--} + \mathbf{I_2};$$
$$2\,[Fe(CN)_6]^{---} + SO_3^{--} + 2\,OH^- \rightarrow 2\,[Fe(CN)_6]^{--} + SO_4^{--} + H_2O;$$
$$2\,[Fe(CN)_6]^{---} + PbO + 2\,OH^- \rightarrow 2\,[Fe(CN)_6]^{--} + \mathbf{PbO_2} + H_2O;$$
$$[Fe(CN)_6]^{---} + \mathbf{Fe(OH)_2} + OH^- \rightarrow [Fe(CN)_6]^{--} + \mathbf{Fe(OH)_3};$$
$$2\,[Fe(CN)_6]^{---} + H_2O_2 + 2\,OH^- \rightarrow 2\,[Fe(CN)_6]^{--} + 2\,H_2O + O_2\uparrow.$$

The ferricyanides are even reduced by ammonia, forming nitrogen:

$$6\,[Fe(CN)_6]^{---} + 8\,NH_3 \rightarrow 6\,[Fe(CN)_6]^{--} + N_2\uparrow + 6\,NH_4^+.$$

On account of this reducibility of ferricyanic acid, it is often difficult, sometimes impossible, to detect its presence, particularly in an insoluble compound. If Turnbull's blue is boiled with caustic potash, the residue will consist of a mixture of ferrous and ferric hydroxides, and the solution will contain potassium ferrocyanide. See p. 155.

The behavior of cyanides toward suspended, yellow mercuric oxide is very important. Almost all cyanides, simple or complex, with the exception of potassium cobalticyanide, are completely decomposed by this reagent. Mercuric cyanide and an oxide of the other metal are formed, and the latter, if insoluble, may be separated from the mercuric cyanide by filtration. Thus potassium ferrocyanide is decomposed by mercuric oxide as follows:

$$K_4[Fe(CN)_6] + 3\,\mathbf{HgO} + 3\,H_2O = \mathbf{Fe(OH)_2} + 4\,KOH + 3\,Hg(CN)_2.$$

Prussian blue as follows:

$$Fe_4[Fe(CN)_6]_3 + 9\,\mathbf{HgO} + 9\,H_2O = 3\,\mathbf{Fe(OH)_2} + 4\,\mathbf{Fe(OH)_3} + 9\,Hg(CN)_2.$$

This decomposition of the cyanides by mercuric oxide is often used in quantitative analysis for the separation of metallic cyanides.

9. **Hydrogen Sulfide** reduces alkali ferricyanide to alkali ferrocyanide

$$2\,[Fe(CN)_6]^{---} + H_2S \rightarrow 2\,[Fe(CN)_6]^{--} + 2\,H^+ + S.$$

10. The aqueous solutions of ferricyanides react with boiling water and with carbon dioxide and alkali carbonate in the same manner as ferricyanides.

Behavior of Ferricyanides on Ignition

The ferricyanides are decomposed into iron carbide, cyanide, dicyanogen, and nitrogen:

$$6\,K_3[Fe(CN)_6] = 18\,KCN + 2\,Fe_3C + 10\,C + 3\,(CN)_2 + 6\,N_2.$$

By heating a ferricyanide in a closed tube, dicyanogen is given off, which burns with a reddish flame.

11. **Manganous Chloride.** — A saturated solution of $MnCl_2$ in concentrated hydrochloric acid gives a brownish black coloration owing to the formation of $MnCl_3$. Cf. p. 491.

THIOCYANIC ACID, HCNS

Thiocyanic acid is found in small amounts, in the form of its sodium salt, in saliva and urine.

The free acid is a colorless, unstable liquid, with a penetrating odor. It freezes at 5° and boils at 85°. It is soluble in water and in alcohol. The aqueous solutions are about as strongly acidic as hydrochloric acid, the ionization being nearly complete in dilute solutions. It can be kept better in aqueous solution than in the anhydrous state, but its salts, the thiocyanates, are much more stable than the acid itself. The alkali salts can be prepared from the corresponding cyanides by heating with sulfur:

$$KCN + S = KCNS.$$

They may also be prepared by treating hydrocyanic acid or an alkali cyanide with an alkali polysulfide at ordinary temperatures,

$$KCN + (NH_4)_2S_2 = (NH_4)_2S + KCNS,$$

or by boiling an alkali thiosulfate solution with an alkali cyanide (cf. p. 416):

$$Na_2S_2O_3 + KCN = Na_2SO_3 + KCNS.$$

The easiest way to prepare ammonium thiocyanate is to allow a mixture of 30 cc. concentrated ammonium hydroxide, 30 cc. alcohol and 7 cc. carbon disulfide, to evaporate very slowly on the water bath. First of all, ammonium thiocarbamate is formed

$$CS_2 + 2\,NH_3 = NH_4CS_2NH_2,$$

and during the evaporation this loses hydrogen sulfide:

$$NH_4CS_2NH_2 = NH_4CNS + H_2S\uparrow.$$

Solubility. — Most thiocyanates are soluble in water; exceptions are the silver, mercury, copper, and gold salts. Lead thiocyanate is difficultly soluble in water; on boiling with water it is decomposed.

Reactions in the Wet Way

1. **Dilute Sulfuric Acid** (double normal) causes no reaction.

2. **Moderately Concentrated Sulfuric Acid** (14-normal) decomposes the thiocyanates, with evolution of carbonyl sulfide, which burns with a blue flame:

$$KCNS + 2\,H_2SO_4 + H_2O = KHSO_4 + (NH_4)HSO_4 + COS\uparrow.$$

3. **Concentrated Sulfuric Acid** violently decomposes thiocyanates, with evolution of very disagreeably smelling vapors (*COS, HCOOH, CO_2, SO_2), and deposition of sulfur.*

4. ***Silver Nitrate*** *precipitates white, curdy, silver thiocyanate,*

$$CNS^- + Ag^+ \rightarrow \mathbf{AgCNS},$$

insoluble in dilute nitric acid, soluble in ammonia.

5. **Ferric Salts** *produce a blood-red coloration, due to the formation of non-ionized ferric thiocyanate,*

$$3\,CNS^- + Fe^{+++} \rightarrow Fe(CNS)_3,$$

very soluble in ether (cf. p. 158).

6. **Mercuric Nitrate** precipitates white mercuric thiocyanate,

$$Hg^{++} + 2\,CNS^- + \mathbf{Hg(CNS)_2},$$

very difficultly soluble in water, but readily soluble in an excess of potassium thiocyanate:

$$\mathbf{Hg(CNS)_2} + CNS^- \rightarrow [Hg(CNS)_3]^-.$$

If dry $K[Hg(CNS)_3]$ is heated, the salt expands greatly (Pharaoh's serpents).

7. **Mercuric Chloride** gives a precipitate only after long standing.

8. **Mercurous Nitrate** produces a gray to black precipitate. On adding mercurous nitrate drop by drop to a fairly concentrated solution of potassium thiocyanate, a gray precipitate of metallic mercury is first obtained, and the solution contains potassium mercuric thiocyanate:

$$Hg_2^{++} + 3\,CNS^- \rightarrow [Hg(CNS)_3]^- + \mathbf{Hg}.$$

If the addition of mercurous nitrate is continued until no more mercury is precipitated, and the solution then filtered, the filtrate will contain potassium mercuric thiocyanate; but, on adding still more mercurous nitrate, pure white, mercurous thiocyanate is precipitated:

$$2\,[Hg(CNS)_3]^- + 3\,Hg_2^{++} \rightarrow 2\,Hg^{++} + 3\,\mathbf{Hg_2(CNS)_2}.$$

If, on the other hand, a very dilute solution of potassium thiocyanate is added to a very dilute solution of mercurous nitrate, the white precipitate of mercurous thiocyanate is obtained directly:

$$Hg_2^{++} + 2\,CNS^- \rightarrow \mathbf{Hg_2(CNS)_2}.$$

9. **Cupric Salts.** — On adding a few drops of a solution containing a cupric salt to one of an alkali thiocyanate, the solution is colored emerald-green; and, on further addition of the copper solution, black

cupric thiocyanate is precipitated. If sulfurous acid is added, white cuprous thiocyanate is deposited,

$$2\,Cu^{++} + SO_3^{--} + 2\,CNS^- + H_2O \rightarrow \mathbf{Cu_2(CNS)_2} + 2\,H^+ + SO_4^{--},$$

insoluble in dilute hydrochloric and sulfuric acids.

10. **Cobalt Salts.** — If a solution containing an alkali thiocyanate is treated with a small amount of a cobalt salt, and the solution shaken with a mixture of equal parts amyl alcohol and ether,* the upper layer of alcohol ether separates out azure-blue in color (cf. p. 192). This reaction is analogous to that of cyanic acid upon cobalt salts (cf. p. 365).

11. **Nitric Acid,** even when dilute, causes decomposition and the formation of nitric oxide, carbon dioxide and sulfuric acid:

$$3\,CNS^- + 10\,H^+ + 13\,NO_3^- \rightarrow 16\,NO\uparrow + 3\,CO_2\uparrow + 3\,SO_4^{--} + 5\,H_2O.$$

12. **Zinc** added to an acid solution of a thiocyanate causes the formation of hydrogen sulfide:

$$\mathbf{Zn} + SCN^- + 3\,H^+ \rightarrow Zn^{++} + H_2S\uparrow + HCN\uparrow.$$

Detection of Thiocyanates in the Presence of Halogen and Cyanide

First free the solution from hydrocyanic acid by adding a little sodium bicarbonate, heating to boiling and passing carbon dioxide gas through the solution until the escaping gas led into slightly acid silver nitrate solution gives no turbidity of silver cyanide.

After the removal of the hydrocyanic acid, test for thiocyanate, *in the absence of iodide*, by acidifying with hydrochloric acid and adding a few drops of ferric chloride. *A blood-red coloration shows the presence of thiocyanate.* The test cannot be obtained satisfactorily in the presence of an iodide because it also will react with ferric chloride, causing liberation of free iodine.

If an iodide is present, add a little nitric acid to the solution from which the hydrocyanic acid has been expelled, and precipitate the halogens and thiocyanate by the addition of an excess of silver nitrate solution. After the precipitate has settled, decant off the supernatant solution and wash the precipitate several times by decantation with water. Then shake the precipitate vigorously with 6-normal ammonia solution. This dissolves the chloride and thiocyanate readily, all or a part of the bromide, but no appreciable quantity of silver iodide. Filter and add colorless ammonium sulfide to the filtrate. Filter off the silver sulfide precipitate, add a drop of sodium carbonate solution, evaporate to small volume, acidify with hydrochloric acid, and test for thiocyanate with ferric chloride solution.

Detection of Halogens in the Presence of Thiocyanate

VOLHARD'S METHOD

Treat the nitric acid solution with an excess of silver solution, filter and dry the precipitate with suction. Transfer the precipitate to a porcelain dish and heat*

* Or with amyl alcohol alone.

it on the water bath for 45 minutes with concentrated nitric acid. This causes the complete decomposition of all the thiocyanate,

$$6\,AgCNS + 4\,H_2O + 16\,HNO_3 = 3\,Ag_2SO_4 + 3\,(NH_4)_2SO_4 + 6\,CO_2\uparrow + 16\,NO\uparrow,$$

but the silver halides are not attacked appreciably. Dilute, filter and wash a few times with hot water. Reduce the precipitate with zinc and dilute sulfuric acid (p. 301), filter and test this filtrate according to p. 327.

Or, instead of treating the washed silver precipitate with nitric acid it may be boiled with sulfuric acid (1 : 1) until the precipitate becomes black and collects in a ball:

$$2\,AgCNS + 2\,H_2SO_4 + 3\,H_2O = 2\,NH_4HSO_4 + COS\uparrow + CO_2\uparrow + Ag_2S.$$

Dilute the solution with water, filter off the silver halides and silver sulfide, wash with water, reduce with zinc and sulfuric acid and test for the halogens after boiling off the hydrogen sulfide from the last filtrate.

Remark. — It is always necessary to destroy the thiocyanate before reducing with zinc and sulfuric acid, because otherwise hydrocyanic acid will be formed:

$$2\,AgSCN + 3\,Zn + 6\,H^+ \rightarrow 2\,Ag + 3\,Zn^{++} + 2\,HCN\uparrow + 2\,H_2S\uparrow.$$

According to A. W. Hofmann, *free* thiocyanic acid on being reduced with zinc and acid yields a mixture of thioformaldehyde, methylamine, ammonium salt and hydrogen sulfide.

Testing Commercial Alkali Thiocyanate for Chloride

C. Mann's Method

Dissolve 5 gms. of the alkali thiocyanate in 20 cc. of water and to the solution add 20 gms. of crystallized copper sulfate dissolved in 100 cc. of water. A black precipitate of cupric thiocyanate is formed:

$$Cu^{++} + 2\,CNS^- \rightarrow Cu(CNS)_2.$$

Pass hydrogen sulfide gas through the solution until the precipitate becomes nearly white:

$$2\,Cu(CNS)_2 + H_2S = Cu_2(CNS)_2 + S + 2\,HCNS.$$

Then, when the supernatant blue copper solution begins to get brown, owing to the formation of copper sulfide, stop introducing the hydrogen sulfide gas and allow the liquid to stand a few hours. During this time the thiocyanic acid formed by the above reaction is acted upon by the copper sulfide present, as follows:

$$2\,Cu(CNS)_2 + 2\,CuS \rightarrow 2\,Cu_2(CNS)_2 + 2\,S.$$

Filter and treat the filtrate with silver nitrate. A white precipitate shows chloride to be present.

Remark. — An equally good method is the following: Treat the solution of the thiocyanate with an excess of copper sulfate solution and introduce sulfur dioxide gas until the precipitate becomes white cuprous thiocyanate. Allow the solution to stand several hours, then filter off the cuprous thiocyanate, treat the filtrate with nitric acid and test for chlorine with silver nitrate.

Instead of sulfurous acid, hydroxylamine sulfate may be used to reduce the cupric solution.

Detection of Ferro- and Ferricyanides in the Presence of Thiocyanate

METHOD OF P. E. BROWNING AND H. E. PALMER

Acidify the dilute solution of the alkali salts of these acids with acetic acid or hydrochloric acid, avoiding an excess, and add a solution of thorium nitrate; finely divided thorium ferrocyanide will be precipitated. Shake the solution with finely divided asbestos, or filter paper pulp, filter and wash the precipitate with cold water. Pour dilute sodium hydroxide solution over the precipitate, acidify the solution thus obtained and add a few drops of ferric chloride; *Prussian blue is formed if a ferrocyanide was present.*

Add cadmium sulfate solution to the filtrate from the thorium ferrocyanide precipitate, shake with finely-divided asbestos and filter off the cadmium ferricyanide. Wash the precipitate with cold water, dissolve in sodium hydroxide solution, acidify the solution with hydrochloric acid and treat with ferrous sulfate solution. *The formation of Turnbull's blue shows the presence of ferricyanic acid.*

Add ferric chloride to the filtrate from the cadmium ferricyanide precipitate; *a blood-red coloration will be obtained if a thiocyanate is present.*

Behavior of Thiocyanates on Ignition

The thiocyanates of the alkalies melt readily, and are colored successively yellow, brown, green, and finally blue, becoming white again on cooling.

The thiocyanates of the heavy metals are decomposed into sulfide, splitting off carbon disulfide, dicyanogen, and nitrogen. Thus cuprous thiocyanate is decomposed according to the following equation:

$$4\,Cu_2(CNS)_2 = 4\,Cu_2S + 2\,CS_2\uparrow + 3\,(CN)_2\uparrow + N_2\uparrow.$$

The mercuric thiocyanates swell tremendously on being heated (Pharaoh's serpents).

COBALTICYANIC ACID, $H_3[Co(CN)_6]$

The free acid can be obtained by suspending the lead or copper salt in water and saturating the water with hydrogen sulfide gas; the lead or copper cobalticyanide is changed into less soluble sulfide and, by filtering, an aqueous solution of cobalticyanic acid is obtained from which the solid acid deposits upon evaporation. The free acid may be prepared also by treating the potassium salt with nitric acid, evaporating to dryness on the water bath and extracting the acid with alcohol. After evaporating off the alcohol, needle-shaped, hygroscopic crystals of $H_3[Co(CN)_6]$ are obtained.

Cobalticyanic acid is extremely stable. It is not decomposed by boiling with concentrated hydrochloric or nitric acid, by chlorine or by boiling with HgO. By heating with concentrated sulfuric acid, however, it is decomposed with evolution of carbon monoxide and carbon dioxide:

$$2\,H_3[Co(CN)_6] + 8\,H_2SO_4 + 13\,H_2O = 2\,CoSO_4 + 6\,(NH_4)_2SO_4 + 11\,CO\uparrow + CO_2\uparrow.$$

Solubility of Cobalticyanides. — The alkali, alkaline-earth, ferric and other trivalent metal salts are soluble in water. Most of the other salts with bivalent metals and with heavy metals are insoluble in water and in acids.

Reactions in the Wet Way

1. **Dilute Sulfuric Acid.** No reaction.
2. **Concentrated Sulfuric Acid** decomposes all of the salts with evolution of CO and CO_2 and formation of blue, anhydrous cobaltous salt.
3. **Silver Nitrate** produces a white precipitate insoluble in nitric acid but soluble in ammonia.
4. **Lead Acetate, Ferric Chloride** and **Mercuric Chloride** produce no precipitates.
5. **Cobaltous Nitrate** produces a pink precipitate insoluble in nitric acid but soluble in ammonia.
6. **Nickel Sulfate** gives a blue precipitate insoluble in nitric acid but soluble in ammonia.
7. **Copper Sulfate** produces a light-blue precipitate insoluble in nitric acid but forming a blue solution with ammonia.
8. **Cadmium Sulfate** and **Zinc Sulfate** give white precipitates insoluble in nitric acid but soluble in ammonia.
9. **Ferrous Sulfate** produces a white precipitate insoluble in nitric acid.
10. **Mercuric Nitrate** produces a white, voluminous precipitate insoluble in nitric acid.

Reactions in the Dry Way

All the salts of cobalticyanic acid are decomposed by ignition, leaving cyanide and cobalt carbide behind. The alkali and alkaline-earth salts color the borax bead blue in both the oxidizing and reducing flames.

Group II

Silver Nitrate produces a precipitate soluble in nitric acid.
Barium Chloride causes no precipitation.

NITROUS ACID, HNO_2

Occurrence. — Nitrous acid never occurs in nature except in the form of its salts, the nitrites. It is found in the air, as ammonium nitrite and in many soils and waters, particularly in those which are contaminated with ammonia or decaying substances.

Ammonia is oxidized by the action of microörganisms (*monas nitrificans*) to nitrous acid, which combines with more ammonia to form ammonium nitrite.

Preparation of Nitrous Acid and its Salts. — Nitrous acid is formed by the gentle reduction of nitric acid. If zinc is allowed to act upon dilute nitric acid for a short time, the latter is reduced to nitrous acid,

$$Zn + 3\,HNO_3 \rightarrow Zn(NO_3)_2 + HNO_2 + H_2O,$$

but the reduction can easily go a little farther, forming NO, N_2O, and N_2; while by long-continued action of the zinc, hydroxylamine, NH_2OH, or even ammonia is formed.

If nitric acid of sp. gr. 1.3 is heated with arsenious acid, starch, etc., a mixture of nitric oxide and nitrogen peroxide is obtained, which, on cooling to $-21°$ C., condenses to a bluish-green liquid, N_2O_3, the anhydride of nitrous acid.

If the anhydride is treated with ice-cold water, a bluish-green liquid is obtained, which contains nitrous acid, but always in company with nitric acid; for N_2O_3 unites with water, forming nitrous and nitric acids, and nitric oxide:

$$2\,N_2O_3 + H_2O = HNO_3 + HNO_2 + 2\,NO.$$

At a higher temperature nitrous acid is gradually changed into nitric acid:

$$3\,HNO_2 = HNO_3 + 2\,NO + H_2O.$$

Pure nitrous acid, therefore, is not known. In aqueous solution it exists as a fairly strong acid, the ionization constant being 0.45×10^{-3}; it is ionized about twenty times as much as acetic acid in 0.1-normal solution.

If the above mixture of nitric oxide and nitrogen peroxide is conducted into concentrated sulfuric acid, the two gases are readily absorbed, forming nitrosyl sulfuric acid:

$$2\,H_2SO_4 + NO + NO_2 \rightarrow H_2O + 2\,H(NO)SO_4.$$

This solution of nitrosyl sulfuric acid in sulfuric acid is sometimes called "nitrose."

If the solution is added to cold water, sulfuric and nitrous acids are formed:

$$H(NO)SO_4 + H_2O \rightarrow HNO_2 + H_2SO_4.$$

A solution of nitrosyl sulfuric acid can be kept indefinitely, so that it is a convenient reagent for the immediate production of nitrous acid at any time.

The salts of nitrous acid, the nitrites, are much more stable than the free acid, and may be obtained by the ignition of nitrates:

$$2\,NaNO_3 = 2\,NaNO_2 + O_2.$$

Nitrites prepared in this way always contain some oxide and some nitrate as impurity.* In order to obtain a pure nitrite, silver nitrite is treated with the calculated amount of a metallic chloride:

$$AgNO_2 + NaCl = AgCl + NaNO_2.$$

The soluble nitrite can be separated from the insoluble silver chloride by filtration.

Solubility of Nitrites. — All nitrites are soluble in water; silver nitrite is difficultly soluble.

Reactions in the Wet Way

As all nitrites are soluble in water, the reactions which serve for the detection of this acid cannot be those of precipitation, but rather those in which a change of color takes place, owing to an oxidation or reduction.

Nitrous acid sometimes acts as an oxidizing agent, and sometimes as a reducing agent.

1. **Dilute Sulfuric Acid** decomposes all nitrites in the cold, setting free brown vapors:

$$(a)\ NaNO_2 + H_2SO_4 = NaHSO_4 + HNO_2;$$
$$(b)\ 3\,HNO_2 = HNO_3 + 2\,NO\uparrow + H_2O;$$
$$(c)\ 2\,NO + O_2\ (\text{air}) = 2\,NO_2\uparrow.$$

2. **Concentrated Sulfuric Acid** reacts exactly the same, but much more violently.

* If the nitrite is heated with a metal, e.g., lead, the reduction takes place at a lower temperature and is almost quantitative.

3. **Silver Nitrate** precipitates from nitrite solutions crystals of silver nitrite in the form of needles, which are slightly soluble in cold water (300 cc. of water dissolve 1 gm. of silver nitrite at the ordinary temperature). In boiling water, silver nitrite is considerably more soluble.

4. **Cobalt Salts** produce (with an excess of potassium nitrite and acetic acid) a yellow crystalline precipitate of potassium cobaltinitrite (cf. p. 191).

5. **Indigo Solution** is completely decolorized by warming with nitrous acid.

6. **Hydriodic Acid** is oxidized by nitrous acid with separation of iodine:

$$2\,I^- + 2\,NO_2^- + 4\,H^+ \rightarrow 2\,H_2O + 2\,NO\uparrow + I_2.$$

If, therefore, a nitrite is added to a solution of potassium iodide and the solution is acidified with sulfuric or acetic acid, the solution becomes yellow, owing to the separation of iodine. If the solution is now shaken with chloroform or carbon disulfide, the latter will be colored reddish-violet. Or, if a little starch paste is added, it will be colored blue by the iodine.

As the above equation shows, hydrogen ions are required in the reaction. If considerable alkali acetate is present, there is no separation of iodine on the addition of acetic acid, but if a few drops of a strong mineral acid are added, iodine is at once set free. This is a good illustration of the mass-action principle (p. 13) and common ion effect (p. 46).

This exceedingly delicate reaction is also caused by the action of a great many other oxidizing agents; and it can only be used for the detection of nitrous acid when it is known that all such oxidizing substances are absent.

As ferric salts also cause liberation of iodine (cf. p. 37) it is evident that nitrous acid cannot be tested for by the above test in the presence of a ferric salt. If, however, a large excess of sodium phosphate is added to the solution, together with a little potassium iodide and some sulfuric acid, no iodine will be liberated by the ferric salt and the presence of a trace of nitrous acid may be detected. The ferric ions are converted into very slightly ionized ferric acid phosphate in this test and the concentration of the ferric ions is made so small that there is no appreciable reaction with the iodide ions. Artmann,* who suggested this procedure, adds 8 gms. $Na_2HPO_4 \cdot 12\,H_2O$, 0.2 gm. KI, 5 cc. 4-normal H_2SO_4 and a little starch solution to 100 cc. of a solution of the ferric salt which is to be tested for nitrite. If as much as 0.3 mg. of N_2O_3 is present, the intense blue color will be obtained immediately.

7. **Ferrous Salts** are oxidized to ferric salts, with evolution of nitric oxide:

$$Fe^{++} + NO_2^- + 2\,H^+ \rightarrow Fe^{+++} + NO\uparrow + H_2O.$$

* *Chem., Ztg.*, **1913**, 501.

The nitric oxide dissolves, in the cold, in the excess of ferrous salt, forming a brown compound of a varying composition: $(FeSO_4)_x(NO)_y$.

To obtain this compound, add a little acid to a concentrated solution of ferrous sulfate and carefully pour the solution to be tested on top. At the zone of contact between the two solutions the dark-brown coloration will be apparent.

Nitric acid gives the same reaction, but only on the addition of concentrated sulfuric acid. Citric or acetic acid furnishes sufficient H^- ions to give the test with a nitrite.

8. **Potassium Permanganate.** — If nitrous acid is added to a warm (about 40° C.) acid solution of potassium permanganate, the latter will become decolorized, owing to the oxidation of the former to nitric acid:

$$2\,MnO_4^- + 5\,NO_2^- + 6\,H^+ \rightarrow 2\,Mn^{++} + 5\,NO_3^- + 3\,H_2O.$$

In this reaction nitrous acid acts as a reducing agent.

9. Detection of Small Amounts of Nitrous Acid by the Peter Griess Method.* — To detect the small amounts of nitrous acid which may be present in drinking-water, of the above reactions only that of potassium iodide and starch is delicate enough. But as hydrogen peroxide and ferric salts are also likely to be present, both of which cause the separation of iodine from an acid solution of potassium iodide, it is evident that dependence upon this reaction alone would often lead to error.

Consequently, in order to detect the presence of traces of nitrous acid we make use of a reaction which was first proposed by Peter Griess, and which is caused by nitrous acid only. It depends upon the formation of an intensely colored azo dyestuff.

Peter Griess used as his reagent phenylenediamine, whereby a yellow dye, Bismarck brown, is formed. Recently, according to the suggestion of Ilosvay v. Ilosva,† an acetic acid solution of sulfanilic acid and of α-naphthylamine is used instead. According to Lunge,‡ it is best to mix the solutions of the last two reagents.

The reagent is prepared as follows:

1. Dissolve 0.5 gm. of sulfanilic acid in 150 cc. of 2-normal acetic acid.

2. Boil 0.2 gm. of solid α-naphthylamine with 20 cc. of water, pour off the colorless solution from the bluish-violet residue, and add to the colorless solution 150 cc. of 2-normal acetic acid.

Mix the two solutions. The mixture keeps well only when kept in a dark place. It turns reddish if exposed to the light, and cannot be decolorized by shaking with zinc.

Procedure. — Treat about 50 cc. of the water with 2 cc. of the above reagent, and allow it to stand five or ten minutes; it will be colored a distinct red if a trace of nitrous acid is present.

10. **Diphenylamine,** dissolved in concentrated sulfuric acid, is colored intensely blue by nitrous acid. Nitric acid and many other

* *Ber.*, **12** (1879), 427.

† *Bull. chim.* [3] **2**, 317.

‡ *Z. angew. Chemie*, **1889**, Heft 23.

oxidizing substances, such as selenic acid, chloric acid, ferric chloride, etc., will give the same reaction (cf. Nitric Acid).

11. **Brucine** dissolved in concentrated sulfuric acid (according to G. Lunge and A. Lwoff *) gives no reddish coloration when treated with nitrosyl sulfuric acid.

Dry, recrystallized silver nitrite, containing 70.05 per cent silver (theory 70.09), did give with brucine (cf. p. 420), in an atmosphere of carbon dioxide, a weak but nevertheless distinct test for nitric acid, probably due to the presence of traces of nitrate remaining in the silver nitrite. On dissolving 15 mgm. of this same nitrite in water, adding an equivalent amount of sodium chloride and diluting to one liter, a solution of sodium nitrite was obtained, of which 1 cc. added *drop by drop* with *constant stirring* to about 4 cc. of concentrated sulfuric acid yielded a solution of nitrosyl sulfuric acid which gave no sign of a red coloration with a drop of brucine reagent. The test was immediately obtained, however, on adding a trace of nitric acid to this solution.

Brucine, therefore, is a reagent by which nitric acid can be detected in the presence of nitrous acid.

12. **Urea** acts with nitrous acid with evolution of nitrogen and carbon dioxide:

$$CO(NH_2)_2 + 2\,HNO_2 \rightarrow 3\,H_2O + CO_2\uparrow + 2\,N_2\uparrow .$$

In this reaction the nitrogen of the urea, with its negative valence of three, is oxidized by the nitrogen of nitrous acid, which has a positive valence of three. In alkaline solutions free halogens will react with urea, but in acid solutions the reaction with nitrous acid is sensitive and characteristic.

13. **Ammonium chloride,** on being added to a boiling solution of a nitrite in dilute acetic acid, causes evolution of nitrogen gas (cf. p. 103):

$$NH_4^+ + NO_2^- \rightarrow 2\,H_2O + N_2\uparrow .$$

14. **Hydrogen Sulfide** gives a precipitate of sulfur. This forms immediately in acid solutions and very slowly in neutral solutions:

$$2\,NO_2^- + H_2S + 2\,H^+ \rightarrow 2\,NO\uparrow + 2\,H_2O + S.$$

15. **Potassium Thiocyanate** does not react with a neutral or slightly acid solution of a nitrite. On adding a strong mineral acid, however, a dark red color is obtained. This color is similar to that produced by a ferric salt and thiocyanate and is due to an oxidation of the thiocyanate. The addition of alcohol, or gently boiling, destroys the color produced by nitrous acid; shaking with carbon disulfide removes the greater part of the color.

* Z. angew. Chem. **1894**, 345.

16. **Resorcinol,** $C_6H_4(OH)_2$, is useful for the detection of small quantities of nitrous acid dissolved in concentrated sulfuric acid. The test is made as follows:

Take 1 cc. of the concentrated sulfuric acid, add just a trace of resorcinol, and dilute with 5 cc. of water. A mere trace of nitrous acid gives a yellow color.

17. **$MnCl_2$ in 12 NHCl.** See page 486.

18. **Thiourea** reacts with nitrous acid in acetic acid solution to form nitrogen gas and thiocyanic acid:

$$CS(NH_2)_2 + HONO = N_2\uparrow + HCNS + 2\,H_2O.$$

The thiocyanic acid can be detected by the red color produced upon adding a solution of a ferric salt. (Cf. page 487.)

HYDROGEN SULFIDE (HYDROSULFURIC ACID), H_2S

Occurrence and Preparation. — Hydrogen sulfide is found in volcanic regions, in many mineral waters (the so-called "sulfur" waters), and, in general, wherever substances containing sulfur are subject to decay, or when they come in contact with decaying substances. Sulfates are easily changed into sulfides by the action of microörganisms which are present in the air; and this is the reason why many mineral waters containing sulfates smell of hydrogen sulfide after standing some time in a corked flask. If, however, the flask and the cork are sterilized, the water can be kept indefinitely. The formation of hydrogen sulfide from sulfates takes place as follows:

By means of carbonaceous matter (dust, etc.) the sulfate is reduced with the aid of microörganisms, at first to sulfide.

$$Na_2SO_4 + 2\,C = 2\,CO_2 + Na_2S,$$

which is then decomposed by carbonic acid:

$$Na_2S + H_2CO_3 = Na_2CO_3 + H_2S\uparrow.$$

Just as hydrogen sulfide may be made from sodium sulfate by the action of organic matter in a corked flask, so in nature the same process brings about the presence of hydrogen sulfide in many mineral waters.

For laboratory purposes, hydrogen sulfide is prepared similarly by the action of dilute sulfuric or hydrochloric acid upon a sulfide (usually iron sulfide, FeS, on account of its cheapness and stability).

Properties. — Hydrogen sulfide is a colorless gas, with an odor like that of rotten eggs; it is absorbed by water at the ordinary temperatures (one volume water absorbs two to three times its own volume). The saturated solution at 25° is approximately 0.1 molal = 0.2 normal. The higher the temperature, the less the solubility, as with all gases. For the primary ionization: $H_2S \rightleftarrows H^+ + HS^-$, the value of the ionization constant

$$\frac{[H^+] \times [HS^-]}{[H_2S]} = k_1 \text{ is } 0.91 \times 10^{-7}.$$

For the secondary ionization, $HS^- \rightarrow H^+ + S^-$, the value of the constant

$$\frac{[H^+] \times [S^{--}]}{[HS^-]} = k_2 \text{ is } 1.2 \times 10^{-15}.$$

In the saturated solution at 25°, the concentration of the hydrogen ion is about 0.9×10^{-4} moles per liter and of the simple sulfide ion it is only 1.2×10^{-15}. According to the table on p. 57, therefore, a saturated solution of hydrogen sulfide should react acid to phenolphthalien and to azolitmin but not to methyl orange.

The solution of hydrogen sulfide becomes turbid on standing in the air as a result of its oxidation by atmospheric oxygen:

$$2\,H_2S + O_2 = 2\,H_2O + 2\,S.$$

Hydrogen sulfide burns in the air with a bluish flame to water and sulfur dioxide:

$$2\,H_2S + 3\,O_2 = 2\,H_2O + 2\,SO_2.$$

The salts of hydrosulfuric acid are called sulfides.

Solubility of Sulfides. — The sulfides of the alkalies and the hydro- and polysulfides of the alkaline earths are soluble in water. The monosulfides of the alkaline earths, particularly calcium sulfide, CaS, are difficultly soluble in water, but they are gradually changed from contact with water into soluble hydrosulfides:

$$2\,CaS + 2\,H_2O \rightarrow Ca(OH)_2 + Ca(SH)_2.$$

The remaining sulfides are insoluble in water. Of these latter FeS, MnS, and ZnS are decomposed by dilute hydrochloric acid with evolution of hydrogen sulfide; others require concentrated hydrochloric acid, e.g., Sb_2S_3, SnS_2, PbS, NiS, CoS, CdS; while the remaining are insoluble in concentrated hydrochloric acid, but are all soluble in aqua regia with separation of sulfur.

Reactions in the Wet Way

Free hydrogen sulfide, as has been stated, is a very weak acid, being even weaker than carbonic acid. The soluble neutral salts, R_2S, on being dissolved, ionize into metal and sulfide ions,

$$R_2S \rightleftarrows 2\,R^+ + S^{--},$$

but under the influence of water, some of the bivalent sulfur ions are changed to univalent HS^- ions,

$$HOH + S^{--} \rightleftarrows HS^- + OH^-;$$

some of the bivalent sulfide ions remain in solution, and, in fact, more in concentrated solutions than in dilute ones.

As, therefore, an aqueous solution of a sulfide contains both S^{--} ions and SH^- ions, while the solutions of the free acid contain chiefly non-ionized H_2S, it is plain why in many reactions the former react in a somewhat different way from the latter.

1. **Dilute Sulfuric Acid** decomposes all soluble, and some insoluble, sulfides, with evolution of hydrogen sulfide.

2. **Concentrated Sulfuric Acid** decomposes all sulfides, on warming, with evolution of sulfur dioxide and deposition of sulfur:

$$Na_2S + 2\,H_2SO_4 = Na_2SO_4 + 2\,H_2O + SO_2\uparrow + S.$$

But even the sulfur goes over into sulfur dioxide after being heated with the sulfuric acid for some time:

$$2\,H_2SO_4 + S = 2\,H_2O + 3\,SO_2\uparrow.$$

3. **Silver Nitrate** produces, in solutions of hydrogen sulfide and of soluble sulfides, a black precipitate of silver sulfide,

$$2\,Ag^+ + H_2S \rightarrow \mathbf{Ag_2S} + 2\,H^+,$$

insoluble in cold nitric acid, in which, however, it dissolves on warming (cf. p. 190).

4. **Barium Chloride** causes no precipitation.

5. **Lead Salts** (best a solution containing an excess of alkali) produce a black precipitate of lead sulfide. All sulfides which are decomposed by hydrochloric acid evolve hydrogen sulfide, and this gas, on coming in contact with a piece of filter paper moistened with an alkaline lead solution, colors the latter black. An insoluble sulfide (pyrite, arsenic sulfide, mercuric sulfide, etc.) evolves hydrogen sulfide when treated with hydrochloric acid and tin or zinc.

To test an insoluble sulfide, such as the mineral pyrite, place a little finely granulated tin in a test tube, cover it with 6-normal hydrochloric acid and heat gently. Hold a piece of filter paper which has been moistened with sodium plumbite solution * over the escaping vapors. If it blackens, the tin itself contains a little sulfide and cannot be used for the most delicate test. Usually, however, the blackening with tin alone is so slight that an allowance can be made for it. Now add a little of the substance to be tested and a little more tin. A trace of sulfide will cause blackening of the lead acetate paper.

6. **Sodium Nitroprusside,** $Na_2[Fe(CN)_5(NO)] \cdot 2\,H_2O$, is colored reddish-violet by S^{--} ions, but not by SH^- ions. Consequently hydrogen sulfide itself does not give this reaction, except upon the addition of caustic alkali. The reaction is very sensitive, but not so delicate as the one with an alkaline solution of a lead salt.

7. **Methylene Blue.** — This reaction (which was recommended by Emil Fisher †) is the most sensitive of all reactions for detecting the presence of hydrogen sulfide. It is particularly suited for detecting the presence of traces of hydrogen sulfide in mineral waters, even when all other tests give negative results.

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* Lead acetate solution treated with enough sodium hydroxide to dissolve the lead hydroxide that forms first.

† *Ber.*, **16**, 2234.

Treat the solution to be tested for hydrogen sulfide with one tenth of its volume of concentrated hydrochloric acid, add a little dimethylparaphenylendiamine* sulfate, $NH_2 \cdot C_6H_4 \cdot N(CH_3)_2 \cdot H_2SO_4$, from the point of a knife-blade, stir it into the liquid, and when it has dissolved, add one or two drops of a dilute ferric chloride solution.

The formation of methylene blue may be expressed by the following equation:

$$2\,[NH_2 \cdot C_6H_4 \cdot N(CH_3)_2 \cdot HCl] + 6\,Fe^{+++} + S^{--} \rightarrow N\begin{cases} C_6H_3 \begin{cases} -N(CH_3)_2 \\ S \\ =N(CH_3)_2 \\ \quad | \\ \quad Cl \end{cases} \\ C_6H_3 \end{cases} + 6\,Fe^{++} + NH_4^+ + 4\,H^+ + Cl^-.$$

If only 0.02 mgm. of hydrogen sulfide is present in a liter, the blue color is distinctly apparent after half an hour's standing, while the above tests would give negative results.

If too little hydrochloric acid is present, a red coloration is obtained; this is caused by the action of ferric chloride upon a faintly acid solution of dimethylphenylendiamine. If considerable hydrochloric acid is present, the red coloration does not appear.

8. **Oxidizing Agents,** such as the halogens, nitric acid, chromates, permanganates, ferric salts, etc., decompose hydrogen sulfide with separation of sulfur.

9. **Metallic Silver** is blackened by both free hydrogen sulfide and soluble sulfides:

$$4\,Ag + 2\,H_2S + O_2\,(air) = 2\,H_2O + 2\,Ag_2S;$$

$$4\,Ag + 2\,Na_2S + 2\,H_2O + O_2\,(air) = 4\,NaOH + 2\,Ag_2S.$$

If oxygen and water are not present, the above reactions will not take place. A piece of bright silver suspended for fourteen hours in a sulfur spring showed no sign of darkening until it had been exposed to the air for a short time.

Absolutely dry hydrogen sulfide, in the presence of absolutely dry oxygen, acts upon silver at ordinary temperatures only very slowly; it acts instantly if a trace of water is present.

To detect the presence of sulfur in insoluble sulfides, fuse with a little caustic soda (on the cover of a porcelain crucible) to form soluble sodium sulfide:

$$NiS + 2\,NaOH = H_2O + NiO + Na_2S.$$

Some sulfate is always formed by this treatment; but the aqueous solution of the melt will always contain enough alkali sulfide for any of the above tests.

Behavior of the Sulfides on Ignition

Most sulfides remain unchanged when heated out of contact with the air; arsenic and mercuric sulfides sublime.

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* This may also be called para-amino-dimethylaniline sulfate.

The polysulfides lose sulfur, which sublimes. The sulfides of gold and platinum lose sulfur, leaving the metal behind. All sulfides when heated in the air give off sulfur dioxide, which can be recognized by its odor.

The Detection of Sulfur in Non-Electrolytes is usually effected by heating the substance in a glass tube with metallic sodium (cf. p. 312), and testing the aqueous extract of the melt with sodium nitroprusside; or, the residue in the tube may be treated with dilute hydrochloric acid and the escaping gas tested with lead acetate paper for hydrogen sulfide.

The following method of testing for sulfur is very certain. It depends upon the conversion of any sulfur present into the sulfate ion which is tested for barium chloride in hydrochloric acid solution. (Cf. p. 431.) The best way of converting the sulfur into sulfuric acid is to heat with concentrated nitric acid in a sealed tube.* (Carius method, see Vol. II) or, in the case of difficultly volatile substances low in sulfur, by fusion with sodium peroxide in a nickel crucible. Since, however, this last oxidation often takes place with explosive violence, it is best not to use pure sodium peroxide, but to mix it with sodium-potassium carbonate. Mix the substance (from 0.1 to 5 gms. according to the sulfur content) with ten times as much sodium-potassium carbonate and three times as much sodium peroxide and heat in a nickel crucible, with the crucible inserted in a disk of asbestos board to keep the flame of the gas away from the contents; if this precaution is not taken a little sulfate is obtained from the sulfur in the gas. After cooling the melt, dissolve it in water, filter, acidify with hydrochloric acid and test the filtrate for sulfuric acid with barium chloride.

SULFUR, S

M. Pt. = 113.5°–119.5°; B. Pt. 444.5°

Occurrence. — Sulfur is found native in volcanic regions in the form of orthorhombic pyramids, and in the neighborhood of sulfur waters, being formed from the oxidation of some of the hydrogen sulfide which escapes.

Preparation and Properties. — Like the halogens, sulfur is formed by the oxidation of its hydrogen compound:

$$2\,H_2S + O_2 \rightarrow 2\,H_2O + 2\,S.$$

By heating polysulfides or the sulfides of the noble metals (gold and platinum), sulfur is also obtained.

Sulfur exists in three allotropic modifications:

1. As *Orthorhombic Sulfur*, with a melting-point of 113.5° C., obtained by crystallization from solutions below 95°.

2. As *Monoclinic Sulfur*, with a melting-point of 119.5° C., obtained by the solidification of molten sulfur.

3. As *Amorphous Sulfur*, obtained by quickly cooling the molten sulfur after it has become viscous by heating to 250° C., or after it has become a thin liquid after heating to a higher temperature.

Monoclinic sulfur changes gradually into orthorhombic octahedrons; or, in other words, the unsymmetrical form changes into the symmetrical form. This is a general phenomenon:

If a substance exists in two or more crystallographic forms, the more symmetrical form is always the more stable, and the less symmetrical always has a tendency to go over into the more symmetrical form. Thus the unsymmetrical, orthorhombic, yellow mercuric iodide is changed, by rubbing with a glass rod, into symmetrical, tetragonal, red mercuric iodide (cf. p. 208); and, similarly, the orthorhombic form of calcium carbonate, aragonite, changes into hexagonal calcite.

Both of the *crystalline* modifications of sulfur are soluble in carbon disulfide; and, by evaporating the solution, the sulfur always recrystallizes in the form of octahedrons. Amorphous sulfur is insoluble in carbon disulfide.

Commercial "flowers of sulfur" is a mixture of crystalline and amorphous sulfur, and therefore is only partly soluble in carbon disulfide.

Sulfur burns in the air to sulfur dioxide, and, in the presence of "contact substances," such as platinum, oxide of iron, chromic oxide, etc., it is burned to sulfur trioxide also. Consequently the gas from pyrites burners always contains a mixture of the two gases.

Sulfur is insoluble in water, but soluble in hot caustic alkali, forming a thiosulfate and a sulfide:

$$6\,NaOH + 4\,S = 3\,H_2O + Na_2S_2O_3 + 2\,Na_2S.$$

By further action of sulfur the Na_2S is changed into Na_2S_2, Na_2S_5, etc.

This reaction is entirely analogous to the formation of hypochlorite and chloride by the action of chlorine upon cold dilute caustic alkali:

$$2\,NaOH + Cl_2 = H_2O + NaOCl + NaCl.$$

Sulfur dissolves on warming with an alkali sulfide, forming polysulfides:

$$Na_2S + S = Na_2S_2;$$

$$Na_2S + 4\,S = Na_2S_5.$$

Sulfur is also soluble in alkali sulfites, forming a thiosulfate:

$$Na_2SO_3 + S = Na_2S_2O_3.$$

Hot, concentrated nitric acid, bromine and hydrochloric acid, aqua regia and a mixture of potassium chlorate and hydrochloric acid gradually attack sulfur forming sulfuric acid.

Acetic Acid, $HC_2H_3O_2$

Acetic acid is found in the sap of many plants, partly free and partly in the form of its potassium or calcium salt.

It is formed by the dry distillation of wood or by the oxidation of alcohol.

Anhydrous acetic acid (glacial acetic acid) solidifies below +16° C., forming colorless, glistening plates. It has a penetrating odor, similar to that of sulfur dioxide, and is miscible with water, alcohol, and ether in every proportion. It boils at 118° C.

The aqueous solution reacts as a weak acid. The ionization constant at 25° is 1.8×10^{-5}; in 0.1-normal solution it is a little over one per cent ionized. It is a monobasic acid, and its salts, the acetates, are as a rule readily soluble in water; the silver salt is difficultly soluble.

The most important commercial salts of this acid are sodium acetate and lead acetate (sugar of lead), $Pb(C_2H_3O_2)_2 + 3\ H_2O$.

Neutral lead acetate dissolves lead oxide with the formation of soluble basic salts:

$$Pb(C_2H_3O_2)_2 + \mathbf{PbO} + H_2O = 2\,Pb\begin{matrix}-OH\\-C_2H_3O_2\end{matrix};$$

$$Pb(C_2H_3O_2)_2 + 2\,\mathbf{PbO} = Pb\begin{matrix}-O-Pb-C_2H_3O_2\\-O-Pb-C_2H_3O_2\end{matrix}.$$

The solutions of the soluble basic lead acetates, as well as that of neutral lead acetate, yield precipitates of lead carbonate when acted upon by carbon dioxide. For this reason turbid solutions are often obtained when these salts are dissolved in distilled water, because the latter frequently contains carbonic acid. If a drop of acetic acid is added to the turbid solution the precipitate disappears at once.

Reactions in the Wet Way

Use a solution of sodium acetate for the following reactions:

1. **Dilute Sulfuric Acid** sets acetic acid free from its salts; it is quite volatile and can be recognized by its odor.

2. **Concentrated Sulfuric Acid** also sets acetic acid free. If alcohol is added at the same time and the mixture warmed, ethyl acetate is formed,

$$HC_2H_3O_2 + C_2H_5OH = H_2O + \underset{\text{Ethylacetate}}{C_2H_5 \cdot C_2H_3O_2},$$

which can be recognized by its pleasant, fruity odor.

3. **Silver Nitrate** produces, in fairly concentrated solutions, a white crystalline precipitate of silver acetate (100 parts of water dissolve 1.04 parts at 20° C. and 2.52 parts at 80° C.).

4. **Ferric Chloride** colors neutral solutions dark brown, and by boiling the diluted solution, all the iron is precipitated as basic acetate (cf. p. 158).

5. **Mercurous Nitrate** produces a white precipitate of mercurous acetate:

$$Hg_2^{++} + 2\,C_2H_3O_2^- \rightarrow Hg_2(C_2H_3O_2)_2.$$

One gram of the acetate dissolves in 133 cc. of water at 15°. The precipitate is much more soluble in hot water and on cooling it crystallizes out again, appearing gray because of slight reduction in the neutral solution. Mercurous acetate dissolves in an excess of mercurous nitrate solution.

6. **Lead Oxide,** PbO, on being heated with dilute acetic acid is dissolved and if an excess of the oxide is used, the solution contains basic lead acetate and reacts alkaline; on cooling no crystals are obtained.

7. **Mercuric Chloride** gives no precipitation (difference from formic acid).

Reactions in the Dry Way

All acetates are decomposed on ignition, leaving behind either the carbonate, oxide, or the metal itself, and with the evolution of combustible vapors and gases.

The acetates of the alkalies are decomposed into carbonate and acetone:

$$2\,NaC_2H_3O_2 = Na_2CO_3 + (CH_3)_2CO.$$

The acetates of the alkaline earths always leave the metal in the form of its oxide, while the acetates of the noble metals leave a residue of the metal itself.

Cacodyl Reaction. — If a dry acetate (best an alkali acetate) is heated with arsenic trioxide, a very repulsive-smelling and extremely poisonous gas is formed, called cacodyl oxide:

$$4\,NaC_2H_3O_2 + As_2O_3 \rightarrow 2\,Na_2CO_3 + [(CH_3)_2As]_2O + 2\,CO_2.$$

In spite of the sensitiveness of this test, it cannot always be relied on, for many other organic acids, such as butyric and valerianic acids, give similar reactions.

CYANIC ACID, HCNO

This very unstable acid is obtained by heating its polymer, cyanuric acid, $(HCNO)_3$; it is a colorless liquid with a very penetrating, disagreeable odor, which immediately decomposes in aqueous solution, forming ammonium bicarbonate:

$$HCNO + 2\,H_2O \rightarrow \underset{\text{Carbamic acid}}{HCO_2NH_2} + H_2O \rightarrow NH_4HCO_3.$$

The salts of cyanic acid, the cyanates, are much more stable than the free acid, and may be obtained by the oxidation of cyanides.

By simply fusing potassium cyanide in the air, perceptible quantities of potassium cyanate are formed. If, however, potassium cyanide is heated with oxidizing substances, or those which can be readily reduced, it is easy to change the cyanide completely over to cyanate. The cyanates of the alkalies are stable in the dry state, but take on moisture from the air and are gradually changed into alkali bicarbonate and ammonia:

$$KCNO + 2\,H_2O = KHCO_3 + NH_3\uparrow.$$

Solubility of Cyanates. — The cyanates of the alkalies and alkaline earths are soluble in water. Silver, mercurous, lead, and copper cyanates are insoluble in water. All cyanates are soluble in nitric acid.

Reactions in the Wet Way

Use a freshly-prepared, cold solution of potassium cyanate for these reactions.

1. **Dilute Sulfuric Acid** immediately sets cyanic acid free, which decomposes into ammonium salt and carbon dioxide:

$$CNO^- + H^+ \rightarrow HCNO;\quad HCNO + 2\,H_2O \rightarrow NH_4^+ + HCO_3^-;$$
$$HCO_3^- + H^+ \rightarrow H_2O + CO_2.$$

Consequently a strong evolution of carbon dioxide takes place on adding the sulfuric acid. The carbon dioxide always contains small amounts of undecomposed cyanic acid, which is recognizable by its very penetrating odor. The solution will contain ammonium sulfate; if it is warmed with caustic soda, ammonia will be given off.

2. **Concentrated Sulfuric Acid** reacts similarly.

3. **Silver Nitrate** precipitates white, curdy silver cyanate,

$$KCNO + AgNO_3 = KNO_3 + \mathbf{AgCNO},$$

soluble in ammonia and in nitric acid (difference from silver cyanide).

4. **Barium Chloride** produces no precipitation.

5. **Cobalt Acetate** is colored azure blue by a solution of potassium cyanate. The blue potassium cobaltocyanate, $K_2[Co(CNO)_4]$, discovered by Blomstrand,* is formed by this reaction, and is obtained in the form of tetragonal crystals of a dark azure-blue color.

This blue compound dissolves in water with a blue color. If, however, it is subjected to the action of considerable water, the color disappears, the double salt being dissociated into its components:

$$K_2[Co(CNO)_4] \rightleftarrows Co(CNO)_2 + 2\,KCNO.$$

If more potassium cyanate is added to the solution, which has become colorless, the blue color reappears. The same result is reached by adding alcohol.

Almost all commercial potassium cyanide contains some cyanate.

In order to detect the presence of cyanate in the commercial salt, the cyanide must first be expelled, for the cobalt test does not take place in the presence of cyanide.

According to E. A. Schneider,† the test is made as follows:

Dissolve 3 to 5 gms. of the potassium cyanide in 30 to 50 cc. of cold water and pass carbon dioxide into the solution for 60 to 90 minutes; the hydrocyanic acid is expelled, and potassium bicarbonate is formed, while the potassium cyanate is not affected perceptibly:

$$KCN + H_2CO_3 = HCN \uparrow + KHCO_3.$$

Take 1 cc. of the solution, add 25 cc. of absolute alcohol (to precipitate potassium bicarbonate) and filter. Treat the alcoholic filtrate with a few drops of acetic acid and then add a few drops of alcoholic cobalt acetate solution.

If the original cyanide contained 0.5 per cent of potassium cyanate, the blue color can be distinctly recognized, but alkali thiocyanates give the same reaction.

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* *Journal für praktische Chemie* [2], **3**, 206.

† *Ber.*, **1895**, p. 1540.

HYPOPHOSPHOROUS ACID, H_3PO_2

Hypophosphorous acid is obtained by the decomposition of its barium salt with sulfuric acid, or of its calcium salt with oxalic acid. It is a sirup in concentrated solutions, and, like phosphorous acid, is changed on heating out of contact with the air into phosphoric acid and spontaneously inflammable phosphine gas. The acid is monobasic, and is a moderately strong acid although only one of the hydrogen atoms is replaceable by metals. The salts of hypophosphorous acid are obtained by boiling phosphorus with dilute alkali, whereby phosphine is given off:

$$2\,P_4 + 3\,Ba(OH)_2 + 6\,H_2O = 3\,Ba(H_2PO_2)_2 + 2\,PH_3\uparrow;$$
$$P_4 + 3\,KOH + 3\,H_2O = 3\,K(H_2PO_2) + PH_3\uparrow.$$

The phosphine thus obtained is spontaneously combustible owing to the presence of small quantities of liquid phosphine, P_2H_4; it is, however, mixed with considerable hydrogen because the alkali reacts upon the alkali hypophosphite with evolution of hydrogen. See No. 6, below.

Solubility of Hypophosphites. — All hypophosphites are soluble in water.

Reactions in the Wet Way

1. **Dilute Sulfuric Acid.** — No reaction.

2. **Concentrated Sulfuric Acid** reacts with hypophosphites only on warming, and is reduced to sulfur dioxide, which can be recognized by its odor.

3. **Silver Nitrate** gives white silver phosphite which, even at room temperature, is reduced to metallic silver, sometimes with and sometimes without the evolution of hydrogen, according to the relative amounts of the substances reacting:

$$2\,H_2PO_2^- + 2\,Ag^+ + 4\,H_2O \rightarrow 2\,H_3PO_4 + 2\,Ag + 3\,H_2\uparrow,$$
$$H_2PO_2^- + 4\,Ag^+ + 2\,H_2O \rightarrow H_3PO_4 + 4\,Ag + 3\,H^+.$$

4. **Barium Chloride, Calcium Chloride** and **Lead Acetate** causes no precipitation.

5. **Copper,*** **Mercury,** and **Gold Salts** are reduced to metal.

* With copper the reduction may go so far that copper hydride is formed. Cf. WÜRTZ, *Compt. rend.*, **18**, 102.

6. **Concentrated Caustic Potash.** — By boiling with concentrated caustic alkali, the hypophosphites are oxidized, with evolution of hydrogen, to phosphates:

$$H_2PO_2^- + 2\,OH^- \rightarrow PO_4^{---} + 2\,H_2\uparrow .$$

7. **Zinc** in dilute sulfuric acid solution reduces hypophosphorous acid to phosphine (see Phosphorous Acid).

8. **Mercuric Chloride** added in excess to a hot solution causes precipitation of mercurous chloride:

$$4\,HgCl_2 + H_2PO_2^- + 2\,H_2O \rightarrow 2\,\mathbf{Hg_2Cl_2} + 3\,H^+ + H_3PO_4 + 4\,Cl^-.$$

9. **Ammonium Molybdate** and a few drops of sulfurous acid solution give a dark blue precipitate or a blue color. This very sensitive reaction is hindered by the presence of hydrogen sulfide, thiosulfate, chlorate and stannous chloride.

Reactions in the Dry Way

By ignition phosphate and phosphine are obtained:

$$2\,H_3PO_2 \rightarrow H_3PO_4 + PH_3\uparrow ;$$

$$4\,NaH_2PO_2 \rightarrow \mathbf{Na_4P_2O_7} + H_2O\uparrow + 2\,PH_3\uparrow ;$$

$$2\,Ca(H_2PO_2)_2 \rightarrow \mathbf{Ca_2P_2O_7} + H_2O\uparrow + 2\,PH_3\uparrow .$$

HYDRAZOIC ACID, HN_3

Hydrazoic acid is a colorless, mobile liquid with an odor like that of phosphine. Its constitution may be represented by the formula

$$\begin{array}{l} H-N-N \\ \quad\quad \backslash N /\!/ \end{array}.$$

Its vapors attack the mucous membrane and explode violently when brought in contact with a flame. The aqueous solution is colorless and the acid is of approximately the same strength as acetic acid, having the ionization constant 1.9×10^{-5} at 25°. The salts of this acid are called azides. Moreover, just as chlorine can be made to replace the OH group of an organic acid to form an acid chloride, similarly the azide group may be introduced instead of the OH of the carboxyl radical, forming organic azides.

Hydrazoic acid and all of the azides are more or less explosive so that work with them is not unattended with danger. On heating, or by percussion, very violent explosions are obtained.

Hydrazoic acid dissolves metals with the formation of azides and evolution of hydrogen

$$2\,HN_3 + Zn \rightarrow Zn(N_3)_2 + H_2\uparrow,$$

but a part of the hydrazoic acid is reduced to hydrazine, $NH_2 \cdot NH_2$, and ammonia:

$$3\,Zn + 7\,HN_3 \rightarrow 3\,Zn(N_3)_2 + NH_3\uparrow + N_2H_4.$$

Other reducing agents accomplish this formation of ammonia and hydrazine.

Oxidizing agents, especially iodine, cause the formation of nitrogen gas:

$$2\,HN_3 + I_2 \rightarrow 2\,HI + 3\,N_2\uparrow.$$

Ceric salts are well suited to cause decomposition of hydrazoic acid; cerous salts and nitrogen are obtained. Fuming hydriodic acid causes the formation of nitrogen, ammonia and iodine:

$$HN_3 + 2\,HI \rightarrow N_2\uparrow + NH_3 + I_2.$$

Most azides are soluble in water.

Reactions in the Wet Way

1. **Silver Nitrate** in neutral solution gives a white precipitate of silver azide:

$$Ag^+ + N_3^- \rightarrow \mathbf{AgN_3}.$$

The precipitate resembles silver chloride in appearance but it is soluble in dilute nitric acid.

2. **Mercurous Nitrate** and **Lead Nitrate** cause similar azides to precipitate.

3. **Ferric Chloride** gives a characteristic red coloration.

GROUP III

Silver Nitrate produces a white precipitate, soluble in nitric acid.
Barium Chloride does the same.

SULFUROUS ACID, H_2SO_3

Occurrence and Preparation. — Sulfur dioxide, the anhydride of sulfurous acid, is found in the exhalations of active volcanoes, and is formed by the combustion of sulfur or sulfides in the air.

$$S + O_2 = SO_2 \uparrow,$$

$$4\,FeS_2 + 11\,O_2 = 2\,Fe_2O_3 + 8\,SO_2 \uparrow,$$

or by the reduction of sulfuric acid on heating with sulfur, sulfides, carbon, organic substances, and metals:

$$2\,H_2SO_4 + S = 2\,H_2O + 3\,SO_2 \uparrow;$$

$$2\,H_2SO_4 + C = 2\,H_2O + CO_2 \uparrow + 2\,SO_2 \uparrow;$$

$$2\,H_2SO_4 + Cu = 2\,H_2O + CuSO_4 + SO_2 \uparrow.$$

Mercury, silver, tin, etc., act the same as copper.

Sulfur dioxide is also formed by the decomposition of sulfites and thiosulfates with stronger acids:

$$Na_2SO_3 + H_2SO_4 = Na_2SO_4 + H_2O + SO_2 \uparrow;$$

$$Na_2S_2O_3 + H_2SO_4 = Na_2SO_4 + S + H_2O + SO_2 \uparrow.$$

Sulfurous acid may be prepared for laboratory purposes by placing a concentrated solution of sodium bisulfite in a flask and allowing concentrated sulfuric acid to drop upon it. A steady stream of sulfur dioxide will be evolved without warming.

Sulfur dioxide is a colorless gas, having the penetrating odor peculiar to burning sulfur, and is readily soluble in water and alcohol: one vol. water at 15° C. dissolves 45.36 vol. SO_2; one vol. alcohol at 15° C. dissolves 116 vol. SO_2.

The aqueous solution contains sulfurous acid, H_2SO_3. The acid cannot be isolated, as it decomposes on evaporation into water and sulfur dioxide; consequently the free acid is known only in aqueous solution. It is an acid of moderate strength having an ionization constant of 1.7×10^{-2} for the primary ionization and of 5×10^{-6} for the secondary ionization. By neutralization of this solution with alkali hydroxides or carbonates, the comparatively stable sulfites are

obtained. *In solution, sulfites are gradually oxidized to sulfates by dissolved oxygen.*

Solubility of Sulfites. — The sulfites of the alkalies are readily soluble in water; the remaining sulfites are difficultly soluble or insoluble in water, but are all soluble in hydrochloric acid.

Reactions in the Wet Way

1. **Dilute Sulfuric Acid** evolves sulfur dioxide, in the cold, from all sulfites, the gas being easily recognized by its odor.

2. **Concentrated Sulfuric Acid** reacts in the same way, but much more energetically.

3. **Silver Nitrate** produces, in neutral solutions of sulfites or in an aqueous solution of sulfurous acid, a white crystalline precipitate of silver sulfite,

$$SO_3^{--} + 2\,Ag^+ \rightarrow \mathbf{Ag_2SO_3},$$

soluble in an excess of alkali sulfite, forming sodium argentisulfite:

$$\mathbf{Ag_2SO_3} + Na_2SO_3 = 2\,Na[AgSO_3]$$

By boiling this solution the silver is precipitated as a gray metal:

$$2\,[AgSO_3]^- \rightarrow SO_4^{--} + SO_2\uparrow + 2\,\mathbf{Ag}.$$

If water containing silver sulfite in suspension is boiled, half the silver is reduced to metal, while the other half goes into solution as sulfate:

$$2\,\mathbf{Ag_2SO_3} \rightarrow Ag_2SO_4 + SO_2\uparrow + 2\,\mathbf{Ag}.$$

Silver sulfite is soluble in ammonia and in nitric acid.

4. **Barium Chloride** produces no precipitation in an aqueous solution of sulfurous acid, but in neutral sulfite solutions white barium sulfite is precipitated,

$$SO_3^{--} + Ba^{++} \rightarrow \mathbf{BaSO_3},$$

readily soluble in cold, dilute nitric acid. By boiling the solution, barium sulfate is formed slowly and separates out. As sulfites in aqueous solution gradually change to sulfates, commercial sulfites usually contain sulfate. In this case the precipitate produced by barium chloride in acid solution is barium sulfate, which is insoluble in dilute nitric or hydrochloric acid. If the barium sulfate is filtered off and the filtrate is treated with chlorine or bromine water, another white precipitate of barium sulfate is formed, provided a sulfite was originally present:

$$SO_3^{--} + Cl_2 + Ba^{++} + H_2O \rightarrow 2\,H^+ + 2\,Cl^- + \mathbf{BaSO_4}.$$

5. **Strontium and Calcium Salts** behave similarly to the barium salt.

The sulfites of the alkaline earths vary in their solubilities in sulfurous acid and in water.

Calcium sulfite readily dissolves in an excess of sulfurous acid, forming calcium bisulfite:

$$CaSO_3 + H_2SO_3 = Ca(HSO_3)_2.$$

On boiling this solution, sulfur dioxide escapes, and calcium sulfite is reprecipitated.

The strontium salt also dissolves in sulfurous acid, but more difficultly; the barium salt is practically insoluble in sulfurous acid.

SOLUBILITY OF THE ALKALINE-EARTH SULFITES IN WATER

One gram calcium sulfite dissolves in 800 cc. water at 18° C.
One gram strontium sulfite dissolves in 30,000 cc. water at 18° C.
One gram barium sulfite dissolves in 46,000 cc. water at 18° C.

Advantage is taken of the difficult solubility of strontium sulfite in detecting sulfurous acid in the presence of thiosulfuric acid (which see).

6. **Lead Salts** precipitate white lead sulfite, soluble in cold dilute nitric acid; but on boiling the solution lead sulfate is precipitated.

7. **Sodium Nitroprusside and Zinc Sulfate.** — If a neutral sulfite solution is treated with a dilute solution of sodium nitroprusside, a faint pink coloration is produced. If, however, considerable zinc sulfate is added, the coloration becomes a distinct red. The reaction is still more sensitive if a little potassium ferrocyanide is added, a red precipitate being formed (difference from thiosulfuric acid). This reaction, although very delicate, is not so reliable as the precipitation with strontium chloride.

Sulfurous acid is a strong reducing agent.

8. **Iodine Solutions** are decolorized by sulfurous acid:

$$SO_3^{--} + H_2O + I_2 \rightarrow 2\,H^+ + 2\,I^- + SO_4^{--}.$$

Chlorine or bromine water causes a similar reaction.

9. **Acid Potassium Permanganate Solutions** are also decolorized, sulfuric and dithionic acids being formed in varying amounts according to the temperature and concentration.

Under certain conditions the reaction can take place according to the following equations:

$$2\,MnO_4^- + 6\,SO_3^{--} + 8\,H^+ \rightarrow 2\,Mn^{++} + 4\,SO_4^{--} + S_2O_6^{--} + 4\,H_2O.$$

Under other conditions, however, the sulfurous acid can be com-

pletely oxidized to sulfuric acid. Consequently, sulfurous acid cannot be determined quantitatively by means of potassium permanganate.

10. **Chromic Acid** is reduced to green chromic salt:

$$2\,CrO_4^{--} + 3\,SO_3^{--} + 10\,H^+ \rightarrow 2\,Cr^{+++} + 3\,SO_4^{--} + 5\,H_2O.$$

11. **Mercuric Chloride** is unaffected by sulfurous acid at ordinary temperatures; but, on boiling, it is reduced to mercurous chloride,

$$2\,HgCl_2 + SO_3^{--} + H_2O \rightarrow 2\,H^+ + 2\,Cl^- + SO_4^{--} + \mathbf{Hg_2Cl_2},$$

and on adding more sulfurous acid, the mercurous salt is reduced to gray metal.

12. **Mercurous Nitrate** is immediately acted upon by free sulfurous acid and by alkali sulfite solutions, with the formation of a black precipitate.

13. **Gold Solutions** are also reduced.

14. **Zinc,** in dilute hydrochloric acid solution, reduces sulfurous acid to hydrogen sulfide, which can be recognized by its odor and by its turning lead acetate paper black. Zinc and aqueous sulfurous acid also react to form *hydrosulfurous* acid, $H_2S_2O_4$, a very strong reducing agent:

$$\mathbf{Zn} + 2\,SO_3^{--} + 6\,H^+ \rightarrow Zn^{++} + H_2S_2O_4 + 2\,H_2O.$$

15. **Hydrogen Sulfide** decomposes sulfurous acid in dilute solutions. The principal reaction may be expressed by the equation:

$$H_2SO_3 + 2\,H_2S \rightarrow 3\,H_2O + 3\,\mathbf{S},$$

but pentathionic acid, $H_2S_5O_6$, and possibly other thionic acids, may be formed at the same time

$$5\,H_2SO_3 + 5\,H_2S \rightarrow H_2S_5O_6 + 9\,H_2O + 5\,\mathbf{S}.$$

Reactions in the Dry Way

The sulfites of the alkalies, when heated out of contact with the air, are changed to sulfate and sulfide:

$$4\,\mathbf{Na_2SO_3} \rightarrow 3\,\mathbf{Na_2SO_4} + \mathbf{Na_2S}.$$

By heating an alkali sulfite in the closed tube this reaction takes place, and there is no sublimate of sulfur (difference from thiosulfates). If the melt is treated with hydrochloric acid after cooling, hydrogen sulfide is given off freely.

The remaining sulfites are changed, on being heated out of contact with the air, into sulfur dioxide and oxide or metal:

$$\mathbf{CaSO_3} = \mathbf{CaO} + SO_2\uparrow;$$

$$\mathbf{2\,Ag_2SO_3} = \mathbf{4\,Ag} + 2\,SO_2\uparrow + O_2\uparrow.$$

If a sulfite is heated with sodium carbonate on charcoal, sodium sulfide is formed. If the melt is placed upon a bright silver coin and moistened with water, the silver is blackened, owing to the formation of black silver sulfide (Hepar reaction):

$$2\,Na_2SO_3 + 3\,C = 3\,CO_2\uparrow + 2\,Na_2S,$$

and

$$2\,Na_2S + 4\,Ag + 2\,H_2O + O_2 = 4\,NaOH + 2\,Ag_2S.$$

This Hepar reaction takes place with all sulfur compounds, and therefore shows simply the presence of sulfur. The oxygen required in the above reaction is obtained from the atmosphere.

CARBONIC ACID, H_2CO_3

Like sulfurous acid, pure carbonic acid does not exist; it is known only in aqueous solution. Its anhydride, CO_2, is formed by the combustion of carbon and of carbonaceous matter of all kinds, and is found therefore very widely distributed in nature (in small amounts in the atmosphere, and in enormous amounts in volcanic regions, streaming out from fissures in the earth).

Pure air contains 0.35–0.40 per cent of CO_2. In dwelling places the amount increases considerably, owing to breathing and other forms of combustion. If 3 or 4 per cent is present, as is the case in mines sometimes, breathing becomes difficult, and the miners' lamp begins to burn faintly.

Carbon dioxide occurs also in many mineral waters, and (in the liquid state) is found enclosed in quartz, feldspar, etc. As carbonate it exists in enormous quantities as limestone, marble, aragonite, dolomite, etc. Carbon dioxide is a colorless, odorless, slightly acid-tasting gas, with sp. gr. 1.52. Being, therefore, one and one-half times as heavy as air, it can be poured from one vessel into another. Carbon dioxide does not support combustion; a burning candle goes out in air containing 8 to 10 per cent of this gas.*

Carbon dioxide gas is not very soluble in water. At 15° and 760 mm. pressure, 1 liter of water dissolves its own volume of gas. At higher temperatures it is less soluble and it is easy to expel carbon dioxide from a solution. In the aqueous solution, the following equilibria exist

$$CO_2 + H_2O \rightleftarrows H_2CO_3 \rightleftarrows H^+ + HCO_3^-;$$
$$HCO_3^- \rightleftarrows H^+ + CO_3^{--}.$$

The ionization constant for the primary ionization of carbonic acid is 0.0_43 and for the secondary ionization it is $0.0_{10}7$. According to these values, the primary ionization of carbonic acid takes place to about 0.1 per cent and there is present in a liter of saturated carbon dioxide solution at 15° only about 0.0006 mole of hydrogen ions. The secondary ionization, upon which the quantity of CO_3^{--} ions present depends, takes place only to a negligible extent.

When a strong acid is added to the solution, even the primary ionization of carbonic acid is repressed almost completely. Similarly, when hydrogen ions are added to a carbonate, carbon dioxide is formed, even with acetic acid, and the carbon dioxide is easily expelled by heating. Hydrocyanic acid, hydrogen sulfide and boric acid are the only common acids that do not decompose carbonates.

*Carbon dioxide not only fails to support combustion, but it tends to prevent it; hence its use in fire extinguishers. Being formed by the combustion of carbon, the mass-action principle shows that it will tend to stop the reaction much better than an inert gas.

The salts of carbonic acid, the carbonates, are formed:

1. By passing carbon dioxide gas into a solution of a metallic hydroxide:

$$2\,NaOH + CO_2 = H_2O + Na_2CO_3;$$
$$Ba(OH)_2 + CO_2 = H_2O + \mathbf{BaCO_3}.$$

2. By the action of carbon dioxide upon cyanides, sulfides, and borates of the alkalies and alkaline earths.

3. By the ignition of salts of organic acids (cf. p. 84).

An illustration of the preparation of large amounts of carbonate is the production of potash by burning parts of plants (wood, for example, or the residue from the manufacture of beet sugar, the latter being particularly rich in potassium salts).

Solubility of Carbonates. — Of the normal carbonates, only those of the alkalies are soluble in water; and their aqueous solutions react alkaline, owing to hydrolytic decomposition:

$$Na_2CO_3 + H_2O \rightleftarrows 2\,Na^+ + OH^- + HCO_3^-.$$

The aqueous solution of the carbonates of the alkalies, therefore, behaves as if it were a solution of caustic alkali and alkali bicarbonate.

Many carbonates dissolve in an excess of carbonic acid, forming bicarbonates, particularly the alkaline-earth carbonates:

$$\mathbf{CaCO_3} + H_2CO_3 = Ca(HCO_3)_2.$$

By boiling a solution of calcium bicarbonate, the latter is decomposed into water and carbon dioxide, and calcium carbonate is reprecipitated:

$$Ca(HCO_3)_2 = H_2O + CO_2\uparrow + \mathbf{CaCO_3}.$$

Nearly all samples of drinking-water contain calcium or magnesium bicarbonate; they become turbid, therefore, on boiling (boiler scale). Dilute, cold mineral acids decompose all carbonates with effervescence (due to evolution of carbon dioxide gas).

The native carbonates of magnesium and iron (magnesite, siderite, and dolomite) do not effervesce if a lump of the mineral is treated with cold dilute mineral acids, but when reduced to a fine powder they are more readily acted upon; on warming, all carbonates dissolve readily in acid.

Reactions in the Wet Way

1. **Dilute Sulfuric Acid** decomposes all carbonates with effervescence; except with magnesite, siderite, and dolomite, the reaction takes place in the cold.

As the atmosphere always contains carbon dioxide gas, particularly in a laboratory where many gas flames are burning, considerable caution is necessary in testing for a small quantity of carbonic acid. In the first place, if the substance does not effervesce with acid, there is no need to make the test. Moreover, carbon dioxide is odorless and it is absurd to think that effervescence implies the presence of a carbonate when the escaping gas has the odor of hydrogen sulfide or sulfur dioxide.

A simple method of testing is as follows: Place about 1 gm. of the powdered solid in a test-tube, cover it with about 10 cc. of water and boil for about a minute. This serves to expel the air from the substance and from the water. Add a little 6-normal hydrochloric acid and watch closely to see if there is any sign of effervescence. If there is effervescence notice whether the escaping gas has any odor. Dip two stirring rods into barium hydroxide solution, place one of the rods between the second and third finger and the other between the third and fourth and hold one of the rods inside the test-tube, without touching the sides, and the other rod outside. If a carbonate is present, the barium hydroxide on the rod inside the test-tube will become turbid faster than that on the rod held in the air. This test is of no value, however, in the presence of a sulfite which will also cause barium hydroxide to become turbid.

The above test naturally fails to detect traces of carbonate with certainty, but it is satisfactory for all ordinary work except when a sulfite is present. To detect traces of carbonate, even in the presence of a sulfite, the following procedure is useful. Fit a 100 cc. flask with a rubber stopper containing two holes. Through one hole insert a small dropping funnel so that it reaches nearly to the bottom of the flask. Through the other hole insert a right-angled glass tube which serves to lead the escaping gas to a second flask, containing about 5 gms. of chromic acid anhydride, CrO_3, dissolved in a little water and 25 cc. of 6-normal sulfuric acid. This will serve to oxidize any sulfurous acid or hydrogen sulfide that may be set free. Arrange the tubes in this second flask so that the gas passes down to the bottom of the solution and leaves the flask through an exit tube which just reaches below the rubber stopper. Connect this flask in the same way with a third flask and connect the exit tube from this flask with a drying tube filled with soda-lime, to prevent carbon dioxide getting in from the air. Place the powdered substance in the first flask and cover it with 25 cc. of water. With the third flask empty, conduct a stream of air free from carbon dioxide through the apparatus for ten minutes while heating the water in the first flask. This is best accomplished by applying suction at the end of the train and drawing the air through soda-lime in a drying tube which is placed in a rubber stopper that fits the neck of the dropping funnel. Instead of soda-lime, caustic potash solution (1 : 2) may be used to remove the carbon dioxide from the air. When the carbon dioxide has been expelled from the apparatus, close the stop-cock in the dropping funnel, take away the flame, and quickly add about 25 cc. of barium hydroxide solution to the last flask. With the apparatus all connected, introduce 25 cc. of 6-normal sulfuric acid into the dropping funnel and allow it to run slowly into the flask containing the substance. If not enough gas is evolved to produce a turbidity in the barium hydroxide solution, apply gentle suction as before. After a slight vacuum has been produced, *carefully* open the stop-cock of the dropping funnel, with the soda-lime tube in place, and gradually heat the sulfuric acid to boiling. Continue drawing air through the apparatus for fifteen minutes if necessary. In case a very slight turbidity is obtained in the barium hydroxide solution it is best to run a blank on the apparatus with all the reagents, and then repeat the

experiment. If the test does not give a decided result, the presence of carbonate should never be reported.

In this test the chromic acid, which is added to oxidize the sulfurous acid, may be replaced by other oxidizing agents, e.g., hydrogen peroxide or iodine.

2. **Concentrated Sulfuric Acid** reacts in the same way as dilute sulfuric acid, only more violently.

3. **Silver Nitrate** precipitates white silver carbonate, which becomes yellow on the addition of an excess of the reagent. On boiling with considerable water, the carbonate is partly decomposed into brown silver oxide and carbon dioxide; but the carbonic acid is not expelled completely except by heating to 200°. Silver carbonate is very soluble in ammonia and in nitric acid.

4. **Barium Chloride** precipitates white, voluminous barium carbonate, in the cold, which gradually on standing, but more quickly on warming, becomes crystalline and denser.

5. **Lead Chloride** added to an aqueous solution of alkali carbonate or bicarbonate gives a milky, white precipitate of lead carbonate. Free carbonic acid hinders the reaction and acetic acid dissolves the precipitate.

6. **Rosolic Acid** in 0.2 per cent alcoholic solution which has been treated with barium hydroxide solution until a red color begins to appear is decolorized by free carbonic acid.

7. **Nessler's Reagent** will not give the ammonia test in the presence of free carbonic acid or of bicarbonates. This test may be used for the detection of free carbonic acid or of bicarbonate in solution.

Behavior of Carbonates on Ignition

The carbonates of the alkalies melt with but slight decomposition. Barium carbonate is not decomposed on charcoal before the blowpipe, and does not melt; only at a white heat is it decomposed into infusible barium oxide and carbon dioxide. All remaining carbonates are decomposed at the temperature of the blowpipe into oxide and carbon dioxide. The oxides of the noble metals break down into metal and oxygen.

PERCARBONIC ACID, $H_2C_2O_6$

Free percarbonic acid is not known, but its potassium salt is stable in the dry state. When exposed to moisture it decomposes into hydrogen peroxide and potassium bicarbonate:

$$K_2C_2O_6 + 2\ H_2O = H_2O_2 + 2\ KHCO_3.$$

If the salt, which is characterized by its pale blue color, is placed in considerable cold, dilute sulfuric acid, it dissolves with evolution of carbon dioxide and formation of potassium acid sulfate and hydrogen peroxide. The solution gives all the characteristic reactions of hydrogen peroxide.

To distinguish between percarbonic acid and hydrogen peroxide, dissolve 10 gms. of potassium iodide in water and add 0.1 to 0.3 gm. of the finely powdered substance. If potassium percarbonate is present, iodine is at once liberated:

$$C_2O_6^{--} + 2\ I^- \rightarrow 2\ CO_3^{--} + I_2.$$

If only potassium bicarbonate and hydrogen peroxide are present, the liberation of iodine will take place much more slowly.

Silver nitrate and barium chloride, when treated with a percarbonate, give white precipitates which are soluble in dilute nitric acid.

Potassium permanganate is decolorized by percarbonates and much gas is evolved; in neutral solutions manganese dioxide is precipitated:

$$3\ C_2O_6^{--} + 2\ MnO_4^- \rightarrow 4\ CO_3^{--} + 2\ CO_2\uparrow + 2\ MnO_2 + 3\ O_2\uparrow,$$

$$5\ C_2O_6^{--} + 2\ MnO_4^- + 16\ H^+ \rightarrow 2\ Mn^{++} + 10\ CO_2\uparrow + 5\ O_2\uparrow + 8\ H_2O.$$

BORIC (BORACIC) ACID, H_3BO_3

Occurrence. — Boric acid is found native as sassolite; in the form of its sodium salt, as borax or tinkal, $Na_2B_4O_7 \cdot 10\ H_2O$; as boracite, $2\ Mg_3B_8O_{15} + MgCl_2$; and in many silicates, such as axinite, tourmaline, datolite, etc.

Crystallized boric acid forms colorless flakes, with a mother-of-pearl luster, which are soluble in water (100 parts water dissolve 4 parts of boric acid at 15°, and 33 parts at 100°). The aqueous solution reacts acid, and is a poor conductor of electricity; the ionization constant is 1.7×10^{-9} at 18° and 2.3×10^{-9} at 25° for the primary ionization.

By heating boric acid to 100°, it loses one molecule of water and is changed to metaboric acid, HBO_2. The latter loses more water when heated to 160°, forming pyroboric acid, $H_2B_4O_7$; which, on ignition, loses all its water, being changed to the anhydride of boric acid, boron trioxide, which remains as a difficultly-volatile, hygroscopic glass.

The salts of boric acid, the borates, are derived from the meta- and pyroboric acids. The salts of the ortho acid, H_3BO_3, are not known in the pure state.

In a few exceptional cases boron acts as a metal, forming $B(HSO_4)_3$, $(BO)_2SO_4$, BF_3, BPO_4, etc. The last compound is insoluble in water and dilute acids, but dissolves readily in caustic alkalies.

Solubility of Borates. — The borates of the alkalies dissolve in water, and the solution reacts alkaline.

A concentrated solution of borax behaves as if it contained sodium metaborate, free boric acid, and a small amount of caustic alkali:

$$Na_2B_4O_7 + 3\ H_2O \rightleftarrows 2\ NaBO_2 + 2\ H_3BO_3;$$
$$NaBO_2 + 2\ HOH \rightleftarrows NaOH + H_3BO_3.$$

The more dilute the solution, the greater the extent to which the hydrolysis represented by the second equation will take place; so that a very dilute solution of borax will react as if it contained simply sodium hydroxide and free boric acid.

A solution of an alkali borate will behave differently towards reagents, therefore, according to its concentration and temperature.

The remaining borates are difficultly soluble in water, but readily soluble in acids and in ammonium chloride solution.

Reactions in the Wet Way

For these reactions use a borax solution.

1. **Dilute Sulfuric Acid.** — No reaction. Sulfuric or hydrochloric acid added to a concentrated aqueous solution of a borate, often precipitates boric acid.

2. **Concentrated Sulfuric Acid.** — No visible reaction. Most borates are decomposed by sulfuric acid, setting free boric acid, and the latter is capable of coloring the non-luminous gas-flame with a characteristic green tinge.

If, therefore, a little solid borate is placed in the loop of a platinum wire, moistened with concentrated sulfuric acid, and heated at the edge of the Bunsen flame, the characteristic green coloration will be noticed.

A great many natural silicates containing boric acid, when tested in the above manner, will not give this flame coloration. To produce this coloration moisten the mineral with hydrofluoric acid, place a little of it in the loop of a platinum wire, and heat at the outer edge of the flame; if a borate is present the latter will be colored distinctly green, owing to the formation of volatile boron fluoride.

The presence of copper or of barium interferes with this test.

3. **Concentrated Sulfuric Acid and Alcohol.** — If an alkali or alkaline-earth borate is treated in a small dish with methyl alcohol, then with concentrated sulfuric acid, the mixture stirred and the alcohol lighted, a green-bordered flame will appear, due to the formation of boric acid methyl ester, $B(OCH_3)_3$. The test can also be made with ethyl alcohol, in which case ethyl borate, $B(OC_2H_5)_3$, is formed.

4. **Silver Nitrate** produces, in moderately-concentrated, cold borax solutions, a white precipitate of silver metaborate:

$$Na_2B_4O_7 + 3\,H_2O + 2\,AgNO_3 = 2\,NaNO_3 + 2\,H_3BO_3 + 2\,\mathbf{AgBO_2}.$$

On warming, a brown precipitate of silver oxide is obtained:

$$2\,\mathbf{AgBO_2} + 3\,H_2O = 2\,H_3BO_3 + \mathbf{Ag_2O}.$$

From very dilute solutions, in the cold, silver nitrate produces a brown precipitate of silver oxide.

Silver borate is soluble in ammonia and in nitric acid.

5. **Barium Chloride** produces, in fairly concentrated solutions, a white precipitate of barium metaborate:

$$Na_2B_4O_7 + BaCl_2 + 3\,H_2O = 2\,NaCl + 2\,H_3BO_3 + \mathbf{Ba(BO_2)_2},$$

soluble in an excess of barium chloride and in ammonium chloride.

6. **Calcium and Lead Salts** behave like barium chloride.

7. **Turmeric.** — If a piece of turmeric paper is placed in a solution of free boric acid, apparently no change will take place unless considerable quantities of boric and sulfuric acids are present, but if the paper is dried, it becomes reddish brown. If the brown paper is again dipped in the solution of boric acid, the color remains; which is also true if the paper is dipped in a dilute sulfuric or hydrochloric acid solution (difference from the alkali test with turmeric paper). If the reddish-brown paper is moistened with caustic soda or potash solution, the paper becomes bluish black; or, if only a small amount of boric acid is present, grayish blue.

The shade and intensity of the color varies both with the amount of turmeric and with the amount of boric acid; with a very little boric acid, turmeric, and very dilute caustic soda solution a nearly pure violet color is obtained and with considerable boric acid and stronger alkali, a greenish-black color.

Borate solutions, when acidified with dilute hydrochloric acid, give the above reaction. This sensitive and convenient test for boric acid must be used with caution, for acid solutions of zirconic, titanic, tantalic, niobic, and molybdic acids also color turmeric paper brown.

The reaction is much more sensitive if, instead of using the turmeric paper itself, an alcoholic solution of turmeric is used. Place 2 or 3 drops of the yellow solution in a porcelain dish, add the solution to be tested for boric acid, acidify with acetic acid, and evaporate to dryness on the water-bath. If as much as 0.02 mgm. of B_2O_3 is present, the residue is colored a distinct reddish brown, while 0.002 mgm. suffices to cause a visible reaction. (F. Henz.)

8. **Mercuric Chloride** produces a red precipitate of basic mercuric salt. If considerable free boric acid is present there is no precipitation.

Behavior of Borates on Ignition

The hydrated borates of the alkalies melt with effervescence, forming a colorless glass.

This glass has the property of dissolving many metallic oxides when heated, whereby metaborates are formed which are often very characteristically colored (borax beads); thus copper oxide is dissolved, forming a blue glass:

$$Na_2B_4O_7 + CuO = 2\,NaBO_2 + Cu(BO_2)_2.$$

If this bead is heated in the reducing flame (i.e., with carbon) two things can happen:

(*a*) The colored cupric salt is reduced to colorless cuprous salt:

$$4\,NaBO_2 + 2\,Cu(BO_2)_2 + C = CO\uparrow + Na_2B_4O_7\uparrow + 2\,NaBO_2 + Cu_2(BO_2)_2.$$

(*b*) The cupric salt is reduced to metallic copper, so that the bead appears reddish brown and opaque:

$$4\,NaBO_2 + 2\,Cu(BO_2)_2 + C = CO_2\uparrow + 2\,Na_2B_4O_7 + 2\,Cu.$$

PERBORIC ACID, HBO_3

The perborates are all hydrolyzed to a greater or less extent when in contact with water, the aqueous solutions all give the characteristic reactions of hydrogen peroxide and of the metaborate ion.

$$BO_3^- + H_2O \rightarrow BO_2^- + H_2O_2.$$

The typical reactions of the perborate anion are based upon its oxidizing power.

Reactions in the Wet Way

1. **Potassium Dichromate** gives blue perchromic acid, soluble in ether (cf. p. 147). **Chrome alum** solution also gives the blue color when treated with perborate and shaken with ether (difference from percarbonic acid).

2. **Titanium Trichloride** gives a red color. **Cerous chloride** is turned yellow.

3. **Potassium Permanganate** is decolorized; black manganese dioxide is precipitated unless the solution is kept acid.

4. **Manganous, Nickelous** and **Cobaltous** nitrate or sulfate solutions give black precipitates of MnO_2, $Ni(OH)_3$ and $Co(OH)_3$.

5. **Potassium Iodide** gives free iodine only in acid solutions.

OXALIC ACID, $H_2C_2O_4$

Occurrence and Preparation. — Oxalic acid occurs, in the form of its acid potassium and calcium salts, in the sap of many plants.

It is prepared in large amounts by heating sawdust with molten caustic alkali. The resulting potassium salt is precipitated with milk of lime, forming the insoluble calcium salt; and the latter is decomposed with sulfuric acid. Oxalic acid is also formed by the oxidation of innumerable organic substances such as sugar, starch and cellulose (paper), by means of concentrated nitric acid.

It crystallizes from aqueous solutions in the form of colorless monoclinic prisms, $H_2C_2O_4 \cdot 2\ H_2O$.

By allowing the hydrated acid to stand over sulfuric acid, water is lost, and the anhydrous acid remains, which, when heated to about 150° C., sublimes, forming needles. If heated still higher it is completely decomposed into water, carbon dioxide, and carbon monoxide:

$$H_2C_2O_4 = H_2O + CO_2\uparrow + CO\uparrow .$$

The crystallized, hydrated acid is soluble in water, alcohol, or ether: 100 parts water at 20° dissolve 11.1 parts oxalic acid; 100 parts alcohol at 15° dissolve 33.2 parts oxalic acid; 100 parts ether at 15° dissolve 1.5 parts oxalic acid.

Oxalic acid is a fairly strong, dibasic acid, and forms neutral and acid salts, e.g., potassium oxalate, $K_2C_2O_4$; potassium binoxalate, KHC_2O_4; potassium tetroxalate, $KHC_2O_4 \cdot H_2C_2O_4 \cdot 2\ H_2O$.

Solubility. — The oxalates are mostly insoluble in water, with the exception of the oxalates of the alkalies and of magnesium. In an excess of an alkali oxalate many of the insoluble oxalates dissolve. Thus ink spots and rust spots can often be removed from clothing by means of a solution of oxalic acid or of potassium tetroxalate:

$$Fe_2O_3 + 6\ H_2C_2O_4 \rightarrow 2\ H_3[Fe(C_2O_4)_3] + 3\ H_2O.$$

Oxalic acid is also a good solvent for ferric phosphate. All oxalates dissolve readily in mineral acids.

Reactions in the Wet Way

A solution of ammonium oxalate may be used for the following reactions:

1. **Dilute Sulfuric Acid.** — No reaction.

2. **Concentrated Sulfuric Acid,** on warming, acts as a dehydrating agent, causing the evolution of equal volumes of carbon monoxide and carbon dioxide; the former will burn with a blue flame:

$$H_2C_2O_4 \rightarrow H_2O + CO\uparrow + CO_2\uparrow.$$

In the presence of manganese dioxide, all oxalates evolve CO_2 with dilute H_2SO_4:

$$H_2C_2O_4 + \mathbf{MnO_2} + H_2SO_4 = MnSO_4 + 2\,H_2O + 2\,CO_2\uparrow.$$

In the same way CO_2 is given off by the action of $KMnO_4$ and dilute H_2SO_4 upon an oxalate at about 60° C.:

$$2\,KMnO_4 + 5\,H_2C_2O_4 + 3\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 8\,H_2O + 10\,CO_2.$$

3. **Silver Nitrate** precipitates white, curdy silver oxalate,

$$C_2O_4^{--} + 2\,Ag^+ = \mathbf{Ag_2C_2O_4},$$

almost insoluble in water, but readily soluble in ammonia and in nitric acid.

4. **Barium Chloride** precipitates white barium oxalate, soluble in oxalic and acetic acids.

5. **Calcium Chloride** precipitates white calcium oxalate, insoluble in oxalic acid, ammonium oxalate, and acetic acid, but readily soluble in hydrochloric and nitric acids. It is the most insoluble of all oxalates and a precipitate is obtained when **calcium sulfate** is added to a solution of oxalate which is acid with acetic acid.

6. **Lead Salts** precipitate white lead oxalate, soluble in nitric acid.

7. **Manganous Sulfate** or **Chloride** precipitates nearly white crystals of manganous oxalate:

$$Mn^{++} + C_2O_4^{--} + 3\,H_2O \rightarrow \mathbf{MnC_2O_4 \cdot 3\,H_2O}.$$

8. **Manganese Dioxide** mixed with oxalic acid or an oxalate, treated with water and a few drops of concentrated sulfuric acid causes decomposition of the oxalate and vigorous evolution of carbon dioxide:

$$\mathbf{MnO_2} + H_2C_2O_4 + H_2SO_4 \rightarrow MnSO_4 + 2\,CO_2\uparrow + 2\,H_2O.$$

Similarly, if oxalic acid or an oxalate is added to a hot acid solution of permanganate, the oxalate is oxidized to carbon dioxide and the permanganate ion is decolorized:

$$2\,MnO_4^- + 5\,C_2O_4^{--} + 16\,H^+ \rightarrow 2\,Mn^{++} + 10\,CO_2\uparrow + 8\,H_2O.$$

9. **Ferrous Phosphate** in phosphoric acid solution gives a dark yellow color with a warm solution of an oxalate.

10. **Resorcinol,** $C_6H_4(OH)_2$, dissolved in about 100 times its weight of concentrated sulfuric acid, gives a blue coloration when added to a solid oxalate and heated until fumes of sulfuric acid are evolved.

11. **Manganous Sulfate.** A sensitive test for the detection of oxalic acid in the presence of hydrochloric, sulfuric, nitric, phosphoric, acetic, butyric, valeric, citric, tartaric, benzoic and salicylic acid as well as phenol or small quantities of formic acid, is performed as follows:

Dissolve a small crystal (3 to 5 mg.) of manganous sulfate in a few drops of water, add a drop of sodium hydroxide solution, heat somewhat, then cool and add drop by drop the solution of oxalic acid or of oxalate, which is slightly acid with sulfuric acid and free from reducing agents. The precipitate of manganous-manganic hydroxide, which was formed by the action of the sodium hydroxide on the manganese sulfate, dissolves by the action of the oxalic acid and a red coloration is obtained.

12. Oxalates of alkaline earth metals undergo metathesis when boiled with a concentrated solution of **sodium carbonate.** Insoluble alkaline earth carbonate and soluble sodium oxalate are formed and, after filtering, the solution can be tested for oxalate. Such a metathesis does not always succeed with oxalates of some other metals, because, owing to the formation of complex salts, the precipitation of the carbonate is often incomplete; thus nickel oxalate forms a soluble sodium nickel oxalate. In such cases, in order to obtain an aqueous oxalic acid solution from an insoluble oxalate, and to remove the cation which may interfere in the tests, it is best to place a little of the powder in warm water and saturate with hydrogen sulfide; the more insoluble sulfide is formed and the solution contains oxalic acid and hydrogen sulfide:

$$NiC_2O_4 + H_2S \rightarrow NiS + H_2C_2O_4.$$

Behavior of Oxalates on Ignition

All oxalates are decomposed on ignition with slight carbonization. The oxalates of the alkalies and alkaline earths are changed to carbonates, with evolution of carbon monoxide. Stronger ignition causes the formation of more or less oxide, the alkaline earth carbonate being quantitatively changed to oxide by heating over the blast lamp. The oxalates of the noble metals, and of iron, nickel, cobalt, copper, etc., leave the metal itself; the oxide is formed in the case of other metals.

TARTARIC ACID, $H_2C_4H_4O_6$

Occurrence. — Tartaric acid occurs partly free and partly as its acid potassium salt in many fruit saps, particularly in that of the grape.

The free acid crystallizes in clear, monoclinic prisms, without water of crystallization.

Inspection of the structural formula of tartaric acid

$$\begin{array}{l} HO - CH - COOH \\ \quad\quad\quad | \\ HO - CH - COOH \end{array}$$

shows that there are in the molecule two carbon atoms each of which has the four valences satisfied by unlike atoms or groups of atoms. Thus each of these carbon atoms has one valence bond satisfied by H, one by OH, one by COOH and one by CH(OH)COOH. Such an atom of carbon is called an *asymmetric carbon* atom and whenever it occurs there usually exist so-called *stereo-isomeric* compounds, i.e., compounds which have the same chemical composition but differ in the way the atoms are arranged in the molecule.

Isomeric compounds of this nature usually show practically the same chemical properties but can be distinguished physically from one another by the shape of the crystals and by the way in which the plane of polarized light is changed when passed through a solution of the crystals.

There are, on account of the two asymmetric carbon atoms in the tartaric acid molecule, four modifications of this acid which exist and the study of these acids has played an important part in the development of chemical theory. One of these has the atoms arranged around each asymmetric carbon atom in such a way that each causes the plane of polarized light to rotate to the right. This acid, the ordinary tartaric acid, is called *d*-tartaric acid. Another acid has the atoms arranged so that just the opposite effect upon polarized light is produced; it is called *l*-tartaric acid. Crystals of these substances are to one another as mirror images, or as the right glove to the left; both form similar hemihedral crystals but certain surfaces found on the right in one case occur on the left in the other.

The third isomeric modification is that known as $(d + l)$ tartaric acid and is called *glutaric acid*. It consists of an equal quantity of both of the above two acids and is optically inactive. Finally, the fourth isomer is called *meso-tartaric acid* and is optically inactive because the two asymmetric carbon atoms have the groups around them arranged so that one neutralizes the other in the molecule.

Tartaric acid is very readily soluble in water (100 parts water dissolve 132 parts of tartaric acid at 15°) and alcohol, but it is insoluble in ether. It is a fairly strong acid, the ionization constant for the primary ionization being 0.97×10^{-3}, at 25°. The salts are called tartrates.

Solubility. — The neutral alkali tartrates are very soluble in water, as also is sodium acid tartrate, while the potassium acid and the ammonium acid tartrates are difficultly soluble in water.

The remaining tartrates are difficultly soluble in water, but all dissolve, more or less readily, in neutral alkali tartrate solution, forming complex salts. These complex salts often conceal the reactions which are typical of the metal ions contained in them. Thus ammonium hydroxide causes no precipitation in solutions of iron, aluminum, titanium, chromium, antimony and tin tartrates. Complex tartrate ions are also formed with manganese, cobalt, nickel, lead, copper, boron, molybdenum and other elements.

The most important commercial salts of this acid are "cream of tartar," $KHC_4H_4O_6$, "Rochelle salt," $KNaC_4H_4O_6$, and "tartar emetic," $K(SbO)C_4H_4O_6$.

Reactions in the Wet Way

A solution of Rochelle salt (sodium potassium tartrate) may be used for these reactions.

1. **Dilute Sulfuric Acid.** — No reaction.

2. **Concentrated Sulfuric Acid** causes carbonization on warming, with evolution of sulfur dioxide, carbon monoxide, carbon dioxide and other gases. The sulfuric acid becomes brown and there is an empyreumatic odor.

3. **Silver Nitrate** produces no precipitation in a solution of free tartaric acid, but in the solution of a neutral tartrate, a white, curdy precipitate is formed immediately,

$$C_4H_4O_6^{--} + 2\,Ag^+ \rightarrow Ag_2C_4H_4O_6.$$

The precipitate is soluble in nitric acid and in ammonia. By warming the ammoniacal silver solution, metallic silver is deposited. This very important reaction for the detection of tartaric acid is performed in the following manner:

Treat the pure tartrate solution with silver nitrate solution until no further precipitation takes place, add a few drops of sodium hydroxide solution and dilute ammonia drop by drop until the precipitate just dissolves. Place the test-tube containing the solution in water which has been heated to 60–70° C. After standing for about fifteen minutes, the silver will be deposited in the form of a beautiful mirror on the sides of the test-tube. This very delicate reaction cannot be performed with certainty in the presence of other acids. In this case the tartaric acid should first be precipitated as potassium acid tartrate. Concentrate the solution to a small volume, add a little solid potassium carbonate, acidify with strong acetic acid and stir the cold solution vigorously; a precipitate of potassium acid tartrate will form at once if considerable tartrate is present. Filter off the precipitate, wash with a little cold water, and dissolve it in as little caustic soda solution as

possible. In this way a solution is obtained which will readily give the silver mirror on the addition of silver nitrate and treatment as above.

If no precipitate is formed on the addition of the acetic acid, add a little alcohol, which causes the precipitate to form more readily. Filter off the precipitate, wash with diluted alcohol, dry, dissolve in dilute sodium hydroxide, and treat as above. If the alcohol is not removed by drying, a mirror is sometimes formed when tartaric acid is absent.

4. **Calcium Chloride.** — If to a concentrated solution of neutral alkali tartrate, in the absence of ammonium salts, calcium chloride solution is added drop by drop, a white amorphous precipitate is formed which redissolves, forming soluble calcium tartrate anions:

$$2\,C_4H_4O_6^{--} + Ca^{++} \rightarrow [Ca(C_4H_4O_6)_2]^{--}.$$

Only after the addition of enough calcium chloride to decompose completely the alkali tartrate is a permanent precipitate formed, which at first is flocculent, but soon becomes crystalline, consisting of neutral calcium tartrate:

$$[Ca(C_4H_4O_6)_2]^{--} + Ca^{++} \rightarrow 2\,\mathbf{CaC_4H_4O_6}.$$

In dilute solutions the first addition of calcium chloride often produces no precipitation; but after standing some time (or more quickly on rubbing the sides of the test-tube with a glass rod) the crystalline precipitate is deposited, $CaC_4H_4O_6 + 4\,H_2O$. Calcium tartrate is difficultly soluble in water; 100 parts water at 15° C. dissolve 0.0159 part of the crystalline salt, and 100 parts boiling water dissolve 0.0285 part of the salt. The precipitate is soluble in acetic acid (difference from calcium oxalate) and also in a solution of concentrated caustic alkali (free from carbonate), probably forming a complex ion:

$$2\,\mathbf{CaC_4H_4O_6} + 2\,OH^- \rightarrow H_2O + [(CaC_4H_4O_6)_2O]^{--}.$$

On boiling this solution, calcium tartrate is reprecipitated in the form of a voluminous gelatinous precipitate, which again goes into solution on cooling. The presence of ammonium chloride retards the formation of the calcium tartrate, but does not prevent it; after standing some time the precipitate settles out in the form of a heavy crystalline powder (difference from citric acid).

The calcium salt of $(d + l)$ tartaric acid is less soluble than calcium *d*-tartrate and has a silky lustre. The presence of aluminum, ferric or antimonyl ions tends to prevent the formation of calcium tartrate on account of forming complex ions.

5. **Potassium Salts** produce no precipitation in neutral solutions of alkali tartrates; but if the concentrated solution is acidified with acetic acid, a crystalline precipitate of potassium acid tartrate is formed upon stirring vigorously:

$$C_4H_4O_6^{--} + K^+ + H^+ \rightarrow \mathbf{KHC_4H_4O_6}.$$

Potassium acid tartrate is difficultly soluble in water (100 cc. water dissolve 0.45 g. of salt) and in acetic acid, but is readily soluble in mineral acids or in caustic

alkali and alkali carbonate solutions. The precipitate may be dissolved in a little ammonia and the above test with calcium chloride obtained.

If a concentrated solution of free tartaric acid is treated with potassium chloride, a precipitate of potassium acid tartrate is formed in spite of the presence of the hydrochloric acid which is set free. From dilute solutions the precipitate appears only after adding sodium acetate (cf. p. 83).

The presence of considerable boric acid greatly interferes with the formation of the potassium acid tartrate. In such cases add ammonium chloride to the concentrated solution in a test-tube, then some calcium chloride solution, and rub the inside walls of the tube with a stirring rod. If only a little tartaric acid is present it may be necessary to let the solution stand twenty-four hours. Filter off any precipitate that may form, wash it two or three times with alcohol, and dissolve the calcium tartrate in a little freshly-prepared potassium hydroxide solution (1 : 5). Filter and heat the filtrate to boiling. Amorphous calcium tartrate should be precipitated. Another way to identify the tartrate in the first precipitate of calcium tartrate is as follows: Place the washed precipitate in a test-tube, add a crystal of silver nitrate, a few drops of 6-normal ammonium hydroxide, and place the test-tube in hot water; a distinct silver mirror should form if a tartrate is present.

6. **Lead Acetate** produces in neutral solutions a white, flocculent precipitate of lead tartrate, easily soluble in nitric acid and in ammonia.

7. **Magnesia Mixture.** — If a concentrated tartaric acid solution is treated with an excess of magnesia mixture, 10 cc. of strong ammonia and a volume of alcohol equal to that of the solution, then, after shaking and allowing to stand twelve hours, the tartaric acid is precipitated quantitatively as crystalline, basic magnesium tartrate insoluble in 50 per cent alcohol (difference from malic and succinic acids):

$$C_4H_4O_6^{--} + 2\,Mg^{++} + 2\,OH^- + H_2O \rightarrow Mg_2(OH)_2(C_4H_4O_6) \cdot H_2O.$$

Filter off the precipitate obtained in the above test, wash it with 50 per cent alcohol, dry and transfer the precipitate to a test-tube, with the aid of a glass rod. Add a little silver nitrate solution, a slight excess of 6-normal ammonium hydroxide and heat to about 60°. A mirror should form if a tartrate is present.

8. **Ferrous Salt** added in small quantity to free tartaric acid or an alkali tartrate gives with two drops of hydrogen peroxide or a few grains of sodium peroxide, and an excess of tartaric acid, a beautiful violet coloration. The sensitive reaction is not obtained with citric, malic or succinic acids.

9. **Potassium Chromate** solution poured over a crystal of tartaric acid at room temperature gives a purple-violet or black coloration and evolution of carbon dioxide. Citric acid crystals, when tested the same way, give a coffee-brown color. In aqueous solution, tartaric acid will give the test: add a little dilute sulfuric acid to the aqueous acetate solution and one or two drops of potassium chromate or dichro-

mate solution and heat for some time; the yellow color of the chromate changes gradually to bluish-violet.

10. **Ammonium Molybdate** in faintly acid solutions together with a little tartaric acid and one or two drops of hydrogen peroxide in a solution heated to about 60°, gives a coloration at first pale yellow, then green and finally blue.

11. **Resorcinol** in concentrated sulfuric acid (1 : 100) gives a wine-red color when heated with a little solid tartaric acid, or a tartrate, until sulfuric acid fumes are evolved. A mere trace of tartaric acid will give the reaction but nitrates, nitrites, chlorates and other oxidizing agents interfere.

Reactions in the Dry Way

If tartaric acid is heated to 135° C., it melts, and on stronger ignition it is decomposed, leaving a residue of carbon and giving off empyreumatic odors (smell of burnt sugar).

The alkali tartrates are also decomposed by ignition, leaving a residue of carbon and alkali carbonate, which effervesces on treatment with acid.

Ammonium tartrate leaves a residue of carbon, which does not effervesce on treatment with acids. The tartrates of the alkaline earths leave behind a mixture of carbon and carbonate; on very strong ignition the latter is changed to oxide.

The tartrates of those metals whose oxides are reduced by carbon are left in the form of metal (Ag, Pb, Fe, Ni, Co, etc.).

CITRIC ACID, $H_3C_6H_5O_7$

Citric acid is found in nature in the juices of many fruits. It is a tribasic acid, readily soluble in water and in alcohol, but difficultly soluble in ether. The pure acid is a colorless, odorless solid which usually contains three molecules of water of crystallization, $H_3C_6H_5O_7 \cdot 3\ H_2O$. Heated carefully to 55° it loses its water of crystallization and at a higher temperature melts and begins to decompose, giving rise to acid vapors and an odor similar to that obtained with tartaric acid under similar treatment. The aqueous solution is optically inactive and shows fairly strong acid properties, the constant for the primary ionization being 0.82×10^{-3} at 25°. Citric acid is dissolved easily by water and by alcohol but less readily by ether. The clear transparent crystals weather on standing in the air owing to loss of water of crystallization; the crystals become opaque and powdery. Its salts are called citrates.

Solubility. — The citrates of the alkalies are soluble in water, and form, with the insoluble citrates of the heavy metals, very soluble complex salts, whose solutions are not precipitated by alkali hydroxides, alkali carbonates, ammonia, etc.

Reactions in the Wet Way

A solution of potassium citrate may be used.

1. **Dilute Sulfuric Acid.** — No reaction.

2. **Concentrated Sulfuric Acid** on being heated with a citrate, as with most α-hydroxyacids, causes formic acid, HCO_2H, to be formed, which then breaks down into water and CO; at the same time some acetone dicarbonic acid, $(CH_2)_2CO \cdot (CO_2H)_2$, is formed and this breaks down into acetone, $(CH_3)_2CO$, and CO_2.

$$H_3C_6H_5O_7 \rightarrow HCO_2H + (CH_2)_2CO(CO_2H)_2,$$

$$HCO_2H \rightarrow H_2O + CO,\ (CH_2)_2CO(CO_2H)_2 \rightarrow (CH_3)_2CO + 2\,CO_2.$$

A part of the citric acid is carbonized and this causes reduction of the sulfuric acid so that some SO_2 is evolved.

3. **Silver Nitrate** produces in neutral solutions a flocculent precipitate of silver citrate, $Ag_3C_6H_5O_7$, readily soluble in nitric acid and in ammonia. On heating the ammoniacal solution to 60° C., no silver mirror is formed; but on heating the solution to boiling, the silver is gradually deposited.

4. **Barium** or **Calcium Chloride** gives no precipitation in neutral solutions (difference from tartaric acid). If, however, caustic soda solution is added to the solution which contains an excess of calcium chloride, a flocculent precipitate of tertiary calcium citrate is at once formed, insoluble in caustic alkali, but readily soluble in ammonium chloride. On boiling the solution in ammonium chloride, crystalline calcium citrate is precipitated, which is now insoluble in ammonium chloride.

5. **Lime Water** in excess produces no precipitation in cold solutions of neutral citrates; on boiling, there is formed a flocculent precipitate of calcium citrate, which almost entirely redissolves on cooling.

6. **Lead Acetate** precipitates from solutions of the free acid, and those containing neutral salts, amorphous $Pb_3(C_6H_5O_7)_2 \cdot H_2O$.

7. **L. Stahre's Test for Citric Acid.*** — To the solution of free citric acid in water, or to the solution of a citrate in very dilute sulfuric or nitric acid (not hydrochloric) add 2 to 5 drops of tenth-normal permanganate solution and heat a short time at 30° to 40° (the solution must not boil!). As soon as the solution is colored brown, or becomes turbid by the precipitation of a little manganese dioxide, add 1 or 2 drops of ammonium oxalate solution and about 1 cc. of 10 per cent sulfuric acid, which will clear up the solution. Now, add a few drops of bromine water, and a distinct, crystalline precipitate of pentabromacetone will be obtained. The bromine water may also be added before the permanganate solution and sometimes the results are better.

This test is so sensitive that 0.3 mgm. of citric acid in 1 cc. of water can be detected.

The experiment succeeds in the presence of tartaric, malic, oxalic, sulfuric and phosphoric acids, except that a little more permanganate is required.

In the Stahre test the following reactions take place:

(*a*) The permanganate oxidizes the citric acid to acetonedicarboxylic acid with evolution of carbon dioxide:

$$5\,H_3C_6H_5O_7 + 2\,MnO_4^- + 6\,H^+ \rightarrow 5\,CO_2 + 2\,Mn^{++} + 8\,H_2O + 5\,(CH_2)_2CO(CO_2H)_2.$$

(*b*) The acetonedicarboxylic acid reacts with bromine, forming pentabromacetone:

$$(CH_2)_2CO(CO_2H)_2 + 5\,Br_2 \rightarrow 2\,CO_2 + 5\,HBr + C_2HBr_5CO.$$

If the permanganate is allowed to act longer upon the citric acid the acetonedicarboxylic acid is converted gradually into acetone, the reaction taking place more quickly on boiling:

$$(CH_2)_2CO(CO_2H)_2 \rightarrow 2\,CO_2 + (CH_3)_2CO.$$

Acetone itself is not brominated as readily as the acetonedicarboxylic acid, and for this reason care should be taken not to let the temperature rise above 40° during the treatment of the citric acid with permanganate.

The citrates on treatment with bromine, without previous oxidation with permanganate, will also give pentabromacetone:

$$K_3C_6H_5O_7 + 6\,Br_2 = 3\,KBr + 3\,CO_2 + 4\,HBr + C_2HBr_5CO.$$

* L. Stahre, *Z. anal. Chem.*, **36**, 195 (1897); also Alfred Wöhlk, *ibid.*, **41**, 94 (1902).

8. **Mercuric Sulfate.** — Denigès' reagent.* Dissolve 5 gms. HgO in 100 cc. of water and 20 cc. conc. H_2SO_4. Treat the solution of the citrate with 1/20 as much reagent and heat to boiling, then add a few drops of 0.1 N $KMnO_4$ solution. A white crystalline precipitate is formed.

The precipitate has the composition: $Hg_3O_2SO_4 \cdot 2\,[(CH_2)_2CO(CO_2)_2]Hg$ and is a mixture of basic mercuric sulfate and the mercuric salt of acetone dicarboxylic acid. The reaction is very sensitive and enables one to detect 0.5 gm. of citric acid dissolved in a liter of water. The reaction is, however, not peculiar to citric acid but is shown by many other ketonic compounds.

9. Citric acid may be distinguished from oxalic, tartaric, and malic acid by means of the deep blue or green color obtained by the following treatment:

To at least 0.01 g. of citric acid add an excess of ammonium hydroxide (3 cc.) in a piece of ignition tubing closed at one end. Seal the other end of the tubing so that but little empty space is above the liquid and heat 6 hours at 110° to 120°. Cool, break off the end of the tubing and pour the liquid into a shallow porcelain dish. After standing several hours in the light a blue or green product is obtained.

This characteristic coloration may also be obtained as follows: To the citric acid add a little glycerol (a little less than the quantity of citric acid used) and heat gently until the mass begins to swell. Dissolve the residue in ammonia, evaporate off most of the liquid, add a little water and 2 drops of fuming nitric acid which has been diluted with five times as much water. The green color which appears first changes by heating on the water bath to blue. Hydrogen peroxide can be used in place of the nitric acid.

Reactions in the Dry Way

The citrates, on ignition, behave exactly like the tartrates.

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* *Comptes rend.*, **138**, 32; *Z. anal. Chem.*, **38**, 718 (1899); and **40**, 121 (1901).

PHOSPHOROUS ACID, H_3PO_3

Formation. — By the slow combustion of phosphorus in the air phosphorus trioxide is formed which, as it is the anhydride of phosphorous acid, reacts with cold water to form the acid:

$$P_2O_3 + 3\,H_2O = 2\,H_3PO_3.$$

Phosphorous acid is formed much more readily by the action of water on the trihalogen compounds of phosphorus:

$$PCl_3 + 3\,HOH = 3\,HCl + H_3PO_3.$$

The hydrochloric acid is removed by evaporation, and the last traces of uncombined water by heating to 180°. If the mass is then allowed to cool, it solidifies to a crystalline, hygroscopic substance which melts at 70°.

By neutralizing the solution of phosphorous acid with bases, the phosphites are obtained. It is never possible, however, to replace more than two of the hydrogen atoms with metal; so that phosphorous acid is considered to be a dibasic acid. Certain organic compounds are known, however, which are derived from tribasic phosphorous acid, H_3PO_3.

Solubility. — Only the phosphites of the alkalies are soluble in water, but they are all soluble in acid.

Reactions in the Wet Way

A solution of sodium phosphite should be used.

1. **Dilute Sulfuric Acid.** — No reaction.

2. **Concentrated Sulfuric Acid** causes no reaction in the cold; on heating, the phosphorous acid reduces the sulfuric acid to sulfurous acid, easily recognized by the odor,

$$H_3PO_3 + H_2SO_4 = H_3PO_4 + H_2O + SO_2\uparrow.$$

3. **Silver Nitrate** produces at first a white precipitate of silver phosphite,

$$HPO_3^{--} + 2\,Ag^+ \rightarrow \mathbf{Ag_2HPO_3},$$

which in the case of a concentrated solution is changed in the cold to metallic silver; while in dilute solutions this reduction takes place only on warming:

$$\mathbf{Ag_2HPO_3} + H_2O = H_3PO_4 + 2\,\mathbf{Ag}.$$

4. **Barium Chloride** precipitates white barium phosphite, soluble in all acids.

5. **Lead Acetate** precipitates white lead phosphite, insoluble in acetic acid.

6. **Mercuric Chloride** is slowly reduced by phosphorous acid in the cold, but more quickly on warming, to mercurous chloride:

$$2\,HgCl_2 + H_3PO_3 + H_2O = H_3PO_4 + 2\,HCl + \mathbf{Hg_2Cl_2}.$$

If the phosphorous acid is present in excess, the reduction in the hot solution (not in the cold) goes farther, and gray metallic mercury is deposited:

$$Hg_2Cl_2 + H_3PO_3 + H_2O = H_3PO_4 + 2\,HCl + 2\,\mathbf{Hg}.$$

Mercurous Nitrate is reduced to mercury under the same conditions.

7. **Zinc** in sulfuric acid solution reduces phosphorous acid to phosphine:

$$H_3PO_3 + 3\,\mathbf{Zn} + 6\,H^+ \rightarrow 3\,Zn^{++} + 3\,H_2O + PH_3\uparrow.$$

If the phosphine is allowed to act upon a concentrated solution of silver nitrate (1 : 1), or, better still, upon the solid silver nitrate, the latter is colored yellow, as with arsine:

$$PH_3 + 6\,AgNO_3 = \mathbf{PAg_3 \cdot 3\,AgNO_3} + 3\,HNO_3.$$

By the addition of water this yellow compound is decomposed with separation of grayish-white silver:

$$\mathbf{PAg_3 \cdot 3\,AgNO_3} + 3\,H_2O = 3\,HNO_3 + H_3PO_3 + 6\,\mathbf{Ag}.$$

The phosphorous acid is, however, immediately oxidized by the nitric acid to phosphoric acid:

$$3\,H_3PO_3 + 2\,HNO_3 = H_2O + 2\,NO + 3\,H_3PO_4.$$

The mixture of phosphine and hydrogen burns with an emerald-green flame.

8. **Sulfurous Acid** is reduced by phosphorous acid to hydrogen sulfide:

$$3\,H_3PO_3 + H_2SO_3 = 3\,H_3PO_4 + H_2S\uparrow.$$

Sulfur Dioxide in a boiling solution containing phosphite gives sulfur and phosphate:

$$SO_2 + 2\,HPO_3^{--} \rightarrow S + 2\,HPO_4^{--}.$$

9. **Concentrated Potassium Hydroxide Solution** changes a phosphite to phosphate, with evolution of hydrogen,

$$K_2HPO_3 + KOH = K_3PO_4 + H_2\uparrow,$$

but with dilute caustic potash the hydrogen evolution is very slight.

10. **Ammonium Molybdate** gives in hot solution a yellow, crystalline precipitate of $(NH_4)_2HPO_3 \cdot 6\ MoO_3 \cdot 2\ H_2O$.

Reactions in the Dry Way

By ignition, phosphorous acid (like hypochlorous acid) is changed at the cost of its own oxygen to the higher compound, while the oxidizing part of the acid is reduced to its hydrogen compound:

$$3\ HClO = HClO_3 + 2\ HCl;$$
$$4\ H_3PO_3 = 3\ H_3PO_4 + PH_3\uparrow.$$

The phosphates behave similarly:

$$8\ Na_2HPO_3 = 4\ Na_3PO_4 + Na_4P_2O_7 + H_2O + 2\ PH_3\uparrow.$$

METAPHOSPHORIC ACID, HPO_3

The monobasic metaphosphoric acid is obtained by treating phosphorous pentoxide with cold water,

$$P_2O_5 + H_2O = 2\,HPO_3,$$

and also by the strong ignition of orthophosphoric acid:

$$H_3PO_4 = H_2O + HPO_3.$$

Metaphosphoric acid is a colorless, glassy, hygroscopic mass. On boiling its aqueous solution, or slowly in the cold, it adds water to the molecule, and is changed to orthophosphoric acid:

$$HPO_3 + H_2O = H_3PO_4.$$

The metaphosphates are readily obtained by heating the monometallic salts of orthophosphoric acid,

$$NaH_2PO_4 = H_2O + NaPO_3,$$

or by igniting sodium ammonium phosphate:

$$NaNH_4HPO_4 = H_2O + NH_3 + NaPO_3.$$

The meta salts are changed into orthophosphates by boiling the aqueous solution in the presence of mineral acid.

There are at least eight different varieties of metaphosphates corresponding to the general formula $(MPO_3)_n$ in which M is a univalent metal. Most of these have been found to give corresponding polymeric free acids of the type $(HPO_3)_n$.

Solubility. — The metaphosphates of the alkalies and of magnesium are soluble in water; the remaining salts are difficultly soluble or insoluble in water, readily soluble in nitric acid, and in an excess of metaphosphoric acid or an excess of alkali metaphosphate.

Reactions in the Wet Way

Sodium metaphosphate is used for the following tests:

1. **Sulfuric Acid** causes no visible reaction.

2. **Silver Nitrate** precipitates white silver metaphosphate, soluble in ammonia and in nitric acid:

$$PO_3^- + Ag^+ \rightarrow \mathbf{AgPO_3}.$$

3. **Barium Chloride** precipitates voluminous barium metaphosphate, soluble in an excess of sodium metaphosphate, from which

solution ammonia causes no precipitation. Barium sodium dimetaphosphate (or a similar polymetaphosphate) is probably formed.

4. **Magnesium Salts** cause no precipitate from moderately dilute solutions, even on boiling (difference from orthophosphoric acid).

5. **Ammonium Molybdate** produces no precipitate in the cold; but, on boiling the acid solution, metaphosphoric acid is changed to orthophosphoric acid and the characteristic precipitate of ammonium phosphomolybdate is formed.

6. **Albumin Solution** is coagulated by an aqueous solution of the free acid (difference from pyro- and orthophosphoric acids), but not by a solution of alkali metaphosphate, except on the addition of acetic acid.

7. **Zinc in Acid Solution** does not reduce metaphosphoric acid (difference from phosphorous acid).

Behavior in the Dry Way

The alkali metaphosphates, on being fused, form a glassy mass, which has the property of dissolving many metallic oxides, forming orthophosphates with characteristic colors. (See Phosphoric Acid.) By fusion with soda, orthophosphates are formed from metaphosphates

PYROPHOSPHORIC ACID, $H_4P_2O_7$

The tetrabasic pyrophosphoric acid is formed by heating orthophosphoric acid to 213°. It is a soft, glassy mass, readily soluble in water; in aqueous solution it gradually adds water to the molecule and is changed to phosphoric acid, the change taking place quickly on boiling the solution.

The salts of pyrophosphoric acid, the pyrophosphates, are obtained by igniting the dimetallic phosphates:

$$2\,Na_2HPO_4 = H_2O + Na_4P_2O_7.$$

Solubility. — The pyrophosphates of the alkalies are soluble in water; the remaining pyrophosphates are difficultly soluble or insoluble in water, but are all soluble in acids, and some are soluble in an excess of sodium pyrophosphate.

Reactions in the Wet Way

A solution of sodium pyrophosphate is used for these tests.

1. **Sulfuric Acid.** — No reaction.

2. **Silver Nitrate** gives a white, curdy precipitate, soluble in ammonia and in nitric acid.

3. **Barium Chloride** causes a white, amorphous precipitate, soluble in acids.

4. **Magnesium Chloride** produces a white precipitate which is soluble in an excess of the magnesium salt, as well as in an excess of sodium pyrophosphate. By boiling this solution a precipitate is formed, which does not disappear on cooling.

5. **Ammonium Molybdate** produces no precipitation in the cold; but, on warming, yellow ammonium phosphomolybdate is precipitated.

6. **Albumin** is not coagulated by free pyrophosphoric acid (difference from metaphosphoric acid).

7. **Cupric Sulfate** gives a pale blue precipitate.

8. **Cadmium Chloride** gives a white precipitate in acetic acid solutions. Ortho- and metaphosphates do not give these last two reactions.

Behavior in the Dry Way

All pyrophosphates on being fused with sodium carbonate are changed to orthophosphates:

$$Na_4P_2O_7 + Na_2CO_3 = CO_2 + 2\,Na_3PO_4.$$

IODIC ACID, HIO_3

Occurrence. — In sea-water and in Chili saltpetre as potassium iodate.

Formation. — By oxidizing iodine with fuming nitric acid or by the action of chlorine upon iodine suspended in water:

$$3\,I_2 + 10\,HNO_3 = 6\,HIO_3 + 10\,NO + 2\,H_2O;$$

$$I_2 + 6\,H_2O + 5\,Cl_2 = 10\,HCl + 2\,HIO_3.$$

Iodic acid itself is a colorless solid which crystallizes in the orthorhombic system. Its anhydride, I_2O_5, is obtained as a white crystalline powder. Both dissolve in water and on being heated give iodine, oxygen and water as decomposition products. Iodic acid is a strong acid and its solutions are largely ionized.

The most important iodate, KIO_3, is obtained by the action of iodine upon a slightly acid solution of potassium chlorate:

$$5\,KClO_3 + 3\,I_2 + 3\,H_2O = 5\,KIO_3 + HIO_3 + 5\,HCl$$

Iodates are also formed by the action of iodine upon alkali hydroxide solutions:

$$3\,I_2 + 6\,KOH = 5\,KI + KIO_3 + 3\,H_2O.$$

In alkaline solutions iodides are oxidized to iodates by hypochlorites and potassium permanganate.

Solubility. — The iodates of the alkalies are soluble in water, but the remaining iodates are difficultly soluble or insoluble.

Reactions in the Wet Way

1. **Sulfuric Acid.** — Neither dilute nor concentrated sulfuric acid decomposes iodic acid; but if reducing substances are present at the same time (such as hydriodic acid, hydrogen sulfide, ferrous salts, etc.), the iodic acid is reduced, with separation of iodine:

$$IO_3^- + 5\,I^- + 6\,H^+ \rightarrow 3\,H_2O + 3\,I_2.$$

2. **Silver Nitrate** precipitates white, curdy silver iodate, $AgIO_3$, readily soluble in ammonia, but difficultly soluble in nitric acid.

3. **Barium Chloride** precipitates white barium iodate, difficultly soluble in hot water (100 parts of boiling water dissolve 0.6 part of the salt), and only slowly soluble in dilute hydrochloric or nitric acids.

4. **Lead Acetate** precipitates lead iodate, difficultly soluble in water and only slightly soluble in nitric acid.

5. Reducing Agents.

(*a*) *Hydriodic acid* reduces iodic acid, with separation of iodine:

$$IO_3^- + 5\,I^- + 6\,H^+ \rightarrow 3\,H_2O + 3\,I_2.$$

The presence of acid is necessary and the reaction will continue only as long as an appreciable quantity of hydrogen ions is present. Iodide and iodate ions, therefore, cause neutralization of a solution.

If the solution is concentrated, the iodine separates out as a brown powder; dilute solutions are colored yellow. The iodine may be absorbed, with a reddish-violet color, by shaking the aqueous solution with chloroform or carbon disulfide.

(*b*) *Sulfurous acid* also causes separation of iodine, unless a large excess of sulfurous acid is added:

$$2\,IO_3^- + 5\,SO_3^{--} + 2\,H^+ \rightarrow 5\,SO_4^{--} + H_2O + I_2,$$
$$IO_3^- + 3\,SO_3^{--} \rightarrow 3\,SO_4^{--} + I^-.$$

The reduction takes place according to the last reaction when three molecules of sulfurous acid are present to one of iodate; sulfurous acid reacts with free iodine (cf. p. 371).

(*c*) *Zinc dust* (or, better, Devarda's alloy) reduces neutral iodate solutions to iodide.

(*d*) *Hydrogen Sulfide* reacts with iodic acid causing precipitation of sulfur and, at first, iodine is liberated:

$$2\,IO_3^- + 5\,H_2S + 2\,H^+ \rightarrow I_2 + 5\,S + 6\,H_2O,$$

but further addition of hydrogen sulfide causes the disappearance of the iodine:

$$I_2 + H_2S \rightarrow 2\,H^+ + 2\,I^- + S.$$

The entire reaction, therefore, after an excess of hydrogen sulfide has been added, is

$$IO_3^- + 3\,H_2S \rightarrow I^- + 3\,H_2O + 3\,S.$$

Phosphorus, either white or red, reacts energetically with iodic acid even in dilute solutions:

$$P_4 + 4\,IO_3^- + 4\,H_2O \rightarrow 4\,H_2PO_4^- + 2\,I_2.$$

Reactions in the Dry Way

Heated on charcoal the iodates deflagrate, but not so strongly as the chlorates; they are all decomposed on being heated, some with and some without the separation of iodine. Thus all neutral iodates of the alkalies are easily decomposed into iodide and oxygen, while the biiodates set free iodine at the same time:

$$2\,KIO_3 = 2\,KI + 3\,O_2;$$
$$4\,[KIO_3 \cdot HIO_3] = 4\,KI + 11\,O_2 + 2\,H_2O + 2\,I_2.$$

Silver Nitrate produces in neutral solutions a colored precipitate, soluble in nitric acid.

Barium Chloride also produces a precipitate which is soluble in nitric acid.

PHOSPHORIC ACID, H_3PO_4

Orthophosphoric acid is obtained by the oxidation of phosphorus by means of nitric acid, or by boiling the meta- and pyro-phosphoric acids with water.

The anhydride, P_2O_5, is a white substance resembling snow in appearance. Exposed to the air it absorbs water rapidly and is, thus, one of the most efficient drying agents for gases. It is the anhydride of ortho, meta and pyrophosphoric acids.

Orthophosphoric acid, H_3PO_4, forms water-clear crystals which are very hygroscopic and quickly become changed to a sirup by exposure to the air. By very strong heating in an open dish it can be volatilized and the vapors fume in the air. There are but few acids which will not decompose or volatilize upon such strong heating.

Phosphoric acid, and by this name the ortho acid is always meant unless the prefix meta or pyro is used, is tribasic and forms salts in which either one, two or three hydrogen atoms are replaced by metals. Salts like NaH_2PO_4 and $Ca(H_2PO_4)_2$ are called preferably *primary* phosphates, but are often called *dihydrogen* phosphates or *acid* phosphates. Salts like Na_2HPO_4 and $CaHPO_4$ are called *secondary* phosphates; the former is often called *disodium phosphate* and the latter, according to this clumsy nomenclature, would be monocalcium mono-hydrogen phosphate. Salts like Na_3PO_4 and $Ca_3(PO_4)_2$ are *tertiary* phosphates though sometimes called trisodium phosphate and tricalcium phosphate.

The first hydrogen of phosphoric acid corresponds to that of a moderately strong acid (cf. p. 10). The second hydrogen is ionized to about the same extent as the first hydrogen of carbonic acid or hydrogen sulfide and this is enough to give an acid reaction with phenolphthalein but not with methyl orange. The third hydrogen of phosphoric acid is scarcely ionized at all, or only about as much as the second hydrogen of hydrogen sulfide.

If a solution of phosphoric acid is neutralized with caustic soda using methyl orange as indicator, the neutral point will be reached when all the phosphoric acid is converted to primary phosphate or, in other words, when one hydrogen has been neutralized in every molecule of H_3PO_4. With phenolphthalein as an indicator, the solution will be neutral when sodium secondary phosphate is formed.

An aqueous solution of sodium primary phosphate, NaH_2PO_4, is neutral to methyl orange and acid to phenolphthalein, an aqueous solution of sodium secondary phosphate is alkaline to methyl orange, and neutral to phenolphthalein. An aqueous solution of sodium tertiary phosphate is alkaline to all indicators.

A mixture of sodium hydroxide and phosphoric acid made in the proportion of one and one-half molecules of base to one molecule of acid will react acid to phenolphthalein and basic to methyl orange; moreover, it will take just as much half-normal acid to neutralize such a solution with methyl orange as indicator as it does of half-normal alkali to neutralize the solution with phenolphthalein as indicator.

Solubility. — The phosphates of the alkalies are soluble in water, and so are the primary salts of the alkaline earths. The secondary phosphates of the alkaline earths are very difficultly soluble, while the corresponding tertiary phosphates (as well as all other phosphates) are insoluble. All phosphates dissolve in acids (cf. p. 48).

Reactions in the Wet Way

Use a solution of sodium secondary phosphate for these reactions.

1. **Sulfuric Acid,** dilute or concentrated, produces no visible change.

2. **Silver Nitrate** produces a yellow precipitate of silver phosphate (difference from meta- and pyrophosphoric acids),

$$2\,HPO_4^{--} + 3\,Ag^+ = H_2PO_4^- + \mathbf{Ag_3PO_4},$$

readily soluble in nitric acid and in ammonia. The precipitate, therefore, can be formed only in neutral solution.

3. **Barium Chloride** precipitates a white, amorphous phosphate:

$$HPO_4^{--} + Ba^{++} \rightarrow \mathbf{BaHPO_4}.$$

In the presence of ammonia the less soluble tertiary salt is precipitated:

$$2\,HPO_4^{--} + 3\,Ba^{++} + 2\,NH_3 = 2\,NH_4^+ + \mathbf{Ba_3(PO_4)_2}.$$

The barium phosphates (as well as those of the other alkaline earths) are easily dissolved by acids, even acetic acid (difference from aluminium and ferric phosphates). From these acid solutions, ammonia reprecipitates the phosphate.

In pure water $H_2PO_4^-$ is dissociated to about 0,1 per cent, but in the presence of acetic acid to a much less extent. $BaHPO_4$ in contact with water furnishes more HPO_4^{--} ions than does $H_2PO_4^-$ in the presence of acetic acid, therefore $BaHPO_4$ dissolves. Similarly $Ba_3(PO_4)_2$ dissolves in order to establish equilibrium between H^+ and PO_4^{---} ions. Aluminium phosphate is less soluble than barium phosphate and therefore requires a stronger acid to dissolve it.

By adding ammonia the hydrogen ions are neutralized and PO_4^{---} ions are obtained in equilibrium with NH_4^+ ions, and $Ba_3(PO_4)_2$ is reprecipitated.

4. **Magnesia Mixture** (an aqueous solution of ammonium chloride, ammonia, and magnesium chloride) precipitates from very dilute solutions white, crystalline magnesium ammonium phosphate, $\mathbf{MgNH_4PO_4 + 6\,H_2O}$,

$$HPO_4^{--} + Mg^{++} + NH_3 \rightarrow \mathbf{MgNH_4PO_4}$$

which is soluble in all acids, but practically insoluble in dilute 2½ per cent ammonia (cf. p. 78).

5. **Ferric Chloride.** — If a solution of sodium phosphate is treated with ferric chloride, a yellowish-white precipitate of ferric phosphate is formed:

$$HPO_4^{--} + Fe^{+++} \rightleftarrows H^+ + \mathbf{FePO_4}.$$

Hydrogen ions are formed in this reaction and, as might be expected from the mass-action principle, the precipitation of the phosphoric acid is not quantitative unless the greater part of the hydrogen ions are removed. This may be accomplished by adding ammonium acetate, as the hydrogen ions must form non-ionized acetic acid to be in equilibrium with the acetate ions (cf. p. 47).

$$HPO_4^{--} + C_2H_3O_2^- + Fe^{+++} \rightarrow HC_2H_3O_2 + \mathbf{FePO_4}.$$

Moreover, if the reaction takes place in a boiling, dilute solution, the excess of the iron can be precipitated as basic ferric acetate. If the solution is filtered hot, a filtrate is obtained which is free from iron and from phosphoric acid. If, however, it cools, some of the iron goes back into solution and, as ferric phosphate is appreciably soluble in ferric acetate solution, some of the phosphoric acid also goes into solution.

Since ferric phosphate, unlike the phosphates of the alkaline earths, is insoluble in acetic acid, it is evident that phosphoric acid may be removed from a solution of alkaline earth phosphate in acetic acid by adding ferric chloride, an excess of soluble acetate and boiling.

To accomplish this, dissolve the phosphate in as little hydrochloric acid as possible, add ammonium carbonate until a slight permanent precipitate is obtained and dissolve the precipitate by adding one or two drops of 6-normal hydrochloric acid. Add an excess of ammonium acetate and ferric chloride, drop by drop until the solution above the yellowish-white precipitate of ferric phosphate is colored distinctly brown by colloidal ferric hydroxide. Dilute with considerable water, heat to boiling and filter while hot. To detect phosphoric acid in the precipitate dissolve it in nitric acid, evaporate the solution to a small volume and treat with ammonium molybdate solution; a yellow, crystalline precipitate of ammonium phosphomolybdate proves the presence of phosphoric acid. Or, dissolve the iron precipitate in hydrochloric acid, add 2 gms. of tartaric acid to prevent the precipitation of iron, add ammonia in excess and then some magnesium-ammonium chloride mixture. A white precipitate of magnesium ammonium phosphate shows the presence of phosphoric acid.

6. **Ammonium Molybdate,** in large excess, precipitates from nitric acid solutions, in the cold on standing (more quickly on slightly warming) a yellow, crystalline precipitate of ammonium phosphomolybdate:

$$H_3PO_4 + 12\,(NH_4)_2MoO_4 + 21\,HNO_3 =$$
$$= \mathbf{(NH_4)_3PO_4 \cdot 12\,MoO_3} + 21\,NH_4NO_3 + 12\,H_2O.$$

This reaction is analogous to that with arsenic acid (cf. page 246), except that the arsenic compound is formed quickly only at the boiling temperature. The presence of ammonium nitrate greatly facilitates the formation of this precipitate.

Ammonium phosphomolybdate is readily soluble in alkalies and in ammonia,

$$\mathbf{(NH_4)_3PO_4 \cdot 12\,MoO_3} + 23\,OH^- \rightarrow 3\,NH_4^+ + HPO_4^{--} + 12\,MoO_4^{--} + 11\,H_2O,$$

also in an excess of alkali phosphate solutions, forming compounds which contain less molybdenum. It is, therefore, always necessary to prevent the formation of such compounds by the addition of a large excess of ammonium molybdate.

Detection of Phosphorus in Iron and Steel. — Phosphorus is present in iron and steel as iron phosphide, but only to a slight extent (usually less than 0.1 per cent). To detect the phosphorus it is necessary to oxidize it to phosphoric acid and then use one of the above reactions. As, however, very small amounts of phosphorus are present, it is necessary to start with a large amount of the original substance in order to obtain a perceptible phosphorus test. It is best to proceed as follows: Dissolve 5 to 10 gms. of the iron or steel in 60 cc. of 6-normal nitric acid,* evaporate the solution to dryness and ignite over a free flame (with constant stirring) until no more red fumes are given off. All organic matter is thereby destroyed, silicic acid is dehydrated and the oxidation of the phosphorus to phosphoric acid is completed. After cooling, dissolve the oxides in 50 cc. of 12-normal hydrochloric acid (warming gently), evaporate off the excess of acid, dilute and filter off the silica. In the filtrate all the iron and all the phosphoric acid will be found, and the latter may be detected by either the molybdate or the magnesia-mixture reaction. To detect the phosphoric acid according to the former method, evaporate to dryness the filtrate obtained after the removal of the silica, dissolve the residue in as little 6-normal nitric acid as possible, add 50 cc. of ammonium molybdate solution and 15–20 cc. of a 75 per cent ammonium nitrate solution, heat the mixture gently, shake or stir vigorously and allow it to stand an hour. A yellow, crystalline precipitate shows the presence of phosphorus.

To detect the phosphorus according to the magnesia-mixture method, it is necessary first to remove the greater part of the iron. Neutralize the hydrochloric acid filtrate with ammonia, add a saturated solution of sulfur dioxide and boil the solution, whereby the previously dark-colored solution is either decolorized or becomes a light green. Add 20 cc. of 12-normal hydrochloric acid, and boil the solution until the excess of sulfur dioxide is expelled. By this operation all the ferric salt is reduced to ferrous salt. Add a few drops of chlorine water (which forms a little ferric salt), neutralize with ammonia and dilute to about a liter; add 3 cc. of a saturated solution of ammonium acetate, 5 cc. of acetic acid, and heat the solution to boiling. All the ferric salt and all the phosphoric acid will be precipitated in the form of ferric phosphate and basic ferric acetate, while the greater part of the iron remains in solution as ferrous salt. Filter off the light brown precipitate through a small plaited filter, wash it with hot water and dissolve in dilute hydrochloric acid. Evaporate the solution almost to dryness, add 2 gms. of citric (or tartaric) acid (which should be dissolved in as little water as possible), add an excess of ammonia, and precipitate the phosphoric acid by the addition of magnesia mixture. A white, crystalline precipitate shows the presence of phosphoric acid.

7. **Lead Acetate** precipitates white lead phosphate, nearly insoluble in acetic acid:

$$2\,HPO_4^{--} + 3\,Pb^{++} + 2\,C_2H_3O_2^{-} \rightarrow 2\,HC_2H_3O_2 + \mathbf{Pb_3(PO_4)_2}.$$

8. **Zinc,** in acid solutions, does not reduce phosphoric acid (difference from phosphorous and hypophosphorous acids).

* If the iron were dissolved in HCl or H_2SO_4, part or even all of the phosphorus would escape as phosphine. Nitric acid oxidizes the phosphorus to phosphoric acid.

9. **Metastannic Acid.** — If metallic tin is added to a nitric acid solution of phosphoric acid, or a phosphate, the tin is changed to metastannic acid, which unites with the phosphoric acid, forming an adsorption compound. This reaction is often used to remove phosphoric acid from an acid solution without the introduction of cations.

The precipitate has been regarded as metastannic acid and stannic phosphate or as a complex phospho-stannic acid, but Werner Mecklenberg * has shown that the phenomena is one of adsorption rather than true chemical combination. The precipitation of the phosphoric acid can be accomplished by the addition of colloidal stannic hydroxide, previously formed by the treatment of tin with nitric acid. The presence of hydrochloric acid *peptonizes* or dissolves the adsorption compound so that the reaction will not take place if much hydrochloric acid is present. According to Gottermann and Schindhelm,† phosphoric acid can be precipitated from *dilute* hydrochloric solutions by a cold, concentrated, freshly-prepared solution of stannic chloride (2 or 3 g. $SnCl_4$ to 0.5 g. H_3PO_4).

10. **Mercurous Nitrate** precipitates from neutral solutions white mercurous phosphate, soluble in nitric acid but insoluble in acetic acid.

11. **Albumin** is not coagulated by orthophosphoric acid.

Reactions in the Dry Way

The tertiary salts of the alkalies melt without decomposition; the secondary salts lose water and are changed to pyrophosphates while the primary salts form a glassy metaphosphate.

The so-called "salt of phosphorus," or "microcosmic salt," $NaNH_4HPO_4 + 4\ H_2O$, which is much used as a reagent, loses water and ammonia on being fused, forming a clear glass of sodium metaphosphate:

$$NaNH_4HPO_4 \cdot 4\ H_2O = 5\ H_2O \uparrow + NH_3 \uparrow + NaPO_3.$$

If the salt is heated in the loop of a platinum wire, a clear bead is obtained — the so-called "salt of phosphorus" bead.

Just as metaphosphoric acid unites with water, on boiling its solution, forming orthophosphoric acid,

$$HPO_3 + H_2O = H_3PO_4,$$

so sodium metaphosphate dissolves, at the fusion temperature, a great many metallic oxides, forming characteristically colored orthophosphates,

$$NaPO_3 + CuO = NaCuPO_4 \text{ (blue bead)},$$

* *Z. anal. Chem.*, **52**, 293.

† *Ber.*, **49**, 2416. *Z. anal. Chem.*, **56**, 205.

which may be changed in the reducing flame to metaphosphate again:

$$NaCuPO_4 + C = CO + Cu + NaPO_3.$$

Brownish red opaque bead

Many anhydrous phosphates are reduced by heating with magnesium to phosphides, which, on being breathed upon, give the peculiar odor of phosphine:

$$Ca_3(PO_4)_2 + 8\,Mg = 8\,MgO + Ca_3P_2;$$

$$Ca_3P_2 + 6\,H_2O = 3\,Ca(OH)_2 + 2\,PH_3\uparrow.$$

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† *Ber.*, **49**, 2416. *Z. anal. Chem.*, **56**, 205.

discovered by Scheuer.* It is a decisive test only when no other substance is present, such as H_2S, H_3As, H_3Sb, formaldehyde or formic acid, which is capable of reacting with silver nitrate.

Red phosphorus is crystalline (hexagonal, rhombohedral), and is formed by heating ordinary phosphorus to about 250° out of contact with the air. It is not poisonous, is insoluble in carbon disulfide, and does not ignite until heated to 256°. It is non-luminous in the dark, does not oxidize in the air, but is readily oxidized by nitric acid to phosphoric acid.

Light-red phosphorus is obtained, according to Schenk,† by heating a solution of white phosphorus in phosphorus tribromide for hours with a return-flow condenser. The phosphorus which then separates is of a light-red color, is not poisonous, but enters into reaction so readily that it is easily distinguished from red phosphorus. It dissolves in concentrated potassium or sodium hydroxide with a stormy evolution of phosphine, the reaction taking place even more readily than with white phosphorus. When covered with ammonia, it blackens.

Black phosphorus is obtained when red phosphorus and lead are heated together in a sealed tube to a red heat and the mass treated with dilute nitric acid after it is cold; the lead dissolves and leaves the phosphorus as black phosphorus. By heating to 360° it is changed to ordinary phosphorus again.

Phosphorus is found in a great many organic substances. In order to detect its presence, the compound is heated in a sealed tube with fuming nitric acid, which destroys the organic matter and oxidizes the phosphorus to phosphoric acid (detected by any of the above reactions).

Arsenious, arsenic, and chromic acids, which also belong to this group, have already been described on pp. 240, 244 and 146.

Mitscherlich Test for White, Poisonous Phosphorus‡

This sensitive test is based upon the luminescence of white phosphorus when exposed to moist air in the dark. It is used to detect phosphorus in cases of poisoning.

Procedure. — Place the food residues, or finely-cut pieces of the body, in the liter flask *K* (Fig. 24) and add enough water to form a thin paste. Then, while shaking, add tartaric acid to slightly acid reaction, in order to combine with any ammonia present. Connect the tube *R* with the flask and heat the contents of the latter to boiling. Carry out this operation in a dark room. As the vapors condense

* *Ann. Chem. Phys.*, **112**, 214 (1859).

† *Ber.*, **36**, 979 (1903).

‡ *J. pr. Chem.*, **66**, 238 (1855).

in the tube *A*, a greenish luminous zone is visible even when only a few milligrams of phosphorus are present. If larger quantities of phosphorus are at hand, the distillate in the flask *B* contains tiny globules of phosphorus which, by gently heating and rotating the liquid, can be made to collect into a larger drop; the aqueous solution also contains phosphorous acid which can be detected by the method of Blondlot-Dusart (see below).

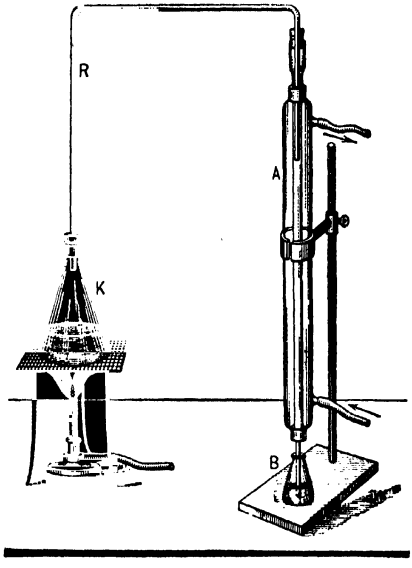

FIG. 24

If, therefore, the luminosity is apparent during the distillation in the dark, then the presence of white phosphorus is probable but not certain, because phosphorus subsulfide, P_4S_3, sometimes used as a substitute for phosphorus in the manufacture of matches, will often cause luminescence in the Mitscherlich apparatus,* especially if a little zinc oxide is added to the liquid in *K* to combine with H_2S, which tends to prevent the luminescence.

If the luminescence is not apparent, it is not certain that white phosphorus is absent; traces of ammonia, hydrogen sulfide, alcohol, ethereal oils and unsaturated hydrocarbons, interfere with the test. In such cases it is advisable not to stop distilling too soon, as it often happens that the interfering substances will distill over and then

* I. MAI and F. SCHAFFER, *Ber.*, **1903**, 870; L. VIGNON, *Bull. soc. chem.* [3], **33**, 805 (1905), and SCHENK and SCHARFF, *Ber.*, **1906**, 1522. All commercial preparations of P_4S_3 do not show luminescence in the Mitscherlich apparatus. Thus a sample from Kahlbaum did not show the slightest luminescence by boiling with water or with concentrated salt solution. It was very pure and contained 55.82 per cent P and 44.14 per cent S.

the luminescence will appear. In case no luminescence is noticed, examine the distillate. Treat a part of it with strong chlorine water, evaporate to small volume on the water-bath and then test for phosphoric acid. Cf. pp. 403 and 404.

According to J. Pesct,* the luminosity is very distinct in the flask if the liquid is heated to boiling, allowed to cool somewhat, and again boiled. In this way 0.004 mgm. of phosphorus can be detected.

Detection of Phosphorus and Phosphorous Acid according to Blondlot-Dusart †

This beautiful method is based upon Dusart's observation that hydrogen containing phosphine, when allowed to flow from a tube provided with a platinum tip, will burn with a flame having an emerald-green core. The green color is particularly apparent upon holding a cold porcelain dish in the flame.

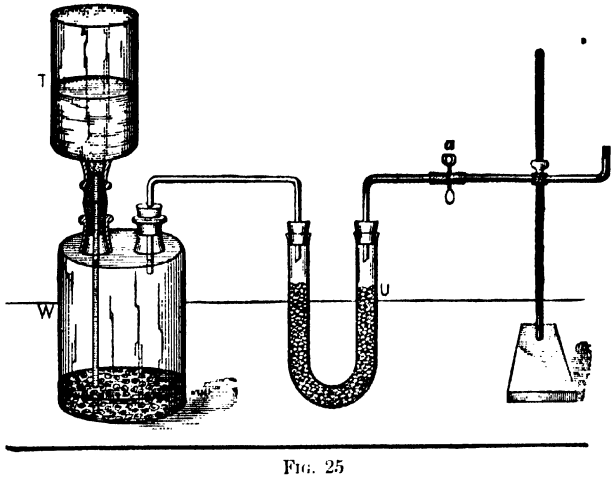

FIG. 25

Since phosphorus, phosphorous acid and hypophosphorous acid (not phosphoric acid) are easily reduced to phosphine by zinc and dilute sulfuric acid, it is merely necessary to pass the evolved gas through a tube with a platinum tip, and light it when the air is all expelled; the merest trace of phosphorus is recognized by the green color.

Inasmuch as organic matter can prevent the appearance of the green flame, the phosphorous is first separated from it as follows: Place the solution containing the phosphorus, or the distillate obtained by the Mitscherlich test, in a gas-evolution flask, add zinc (free from phosphorus) and dilute sulfuric acid (1 : 7), and pass the evolved gas into a neutral solution of silver nitrate; if phosphorus is present a

* *Z. anal. Chem.*, **48**, 35 (1909).

† L. DUSART, *Compt. rend.*, **43**, 1126 (1856), and BLONDLOT, *J. pharm. chim.* [3] **40**, 25 (1854).

black precipitate of silver phosphide is obtained, which, if hydrogen sulfide was present, may contain silver sulfide. Filter off this precipitate, wash it well with water, and place it in the Blondlot apparatus (Fig. 25). In the 500 cc. Woulfe bottle, *W*, generate hydrogen by means of zinc, free from phosphorus, and dilute sulfuric acid (1 : 7). The tube U contains pieces of pumice wet with concentrated potassium hydroxide solution. After the air is entirely expelled from the apparatus, close the pinch-cock *a*, which causes the acid to rise into the reservoir *T* (a bottle with the bottom cut off). Now open the cock *a* wide enough to permit a steady stream of hydrogen to pass out from the delivery tube, which is made of potash-glass and is provided with a platinum tip.* The flame from the lighted gas should not be too large.

If the flame shows no green luminescence in the dark when a porcelain dish is held in it, then the hydrogen gas is free from phosphorus and can be used for the test. Rinse the black silver precipitate through *T* into the bottle *W*. If the precipitate contained phosphorus, the core of the flame becomes green, particularly noticeable upon holding a porcelain dish in it. Any hydrogen sulfide evolved collects in the U-tube, *U*, which contains pumice wet with concentrated caustic potash solution.

Since both the Mitscherlich and the Blondlot-Dusart tests give indications not only of white phosphorus, but also of phosphorus subsulfide, it was desirable to have a test to serve for the identification of white phosphorus with certainty even when the sulfide is also present. For this purpose, R. Schenk and E. Scharff † make use of the property that white phosphorus has of ionizing the atmosphere, a property which the sulfide does not possess. They use the Elster-Geitel apparatus for this purpose. For details of the test the original paper must be consulted.

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* A small blowpipe tip can be used here or, still better, a cylinder made by rolling together some platinum foil.

† R. Schenk and E. Scharff, *Ber.*, **1906**, 1522. For the detection of white phosphorus in the presence of hypophosphorous and arsenious acids see A. Leclive, *Chem. Zentr.*, **1912**, I, 684.

THIOSULFURIC ACID, $H_2S_2O_3$

This very unstable acid, in which one atom of sulfur has a positive valence of six and the other a negative valence of two, is soon decomposed, even in dilute aqueous solution, into sulfurous acid and sulfur:

$$H_2S_2O_3 = H_2SO_3 + S.$$

Free thiosulfuric acid, sometimes called hyposulfurous acid, does not exist.

If the aqueous solution of a thiosulfate is treated with dilute hydrochloric or sulfuric acid, the solution remains clear for a short time; but it soon becomes turbid, owing to the deposition of sulfur, which in this case (unlike most precipitated sulfur) appears yellow.

The salts of thiosulfuric acid, the thiosulfates, are much more stable than the free acid.

Formation of Thiosulfates

1. By boiling sulfur with an alkali or alkaline-earth hydroxide:

$$4\,S + 6\,OH^- \rightarrow 2\,S^{--} + S_2O_3^{--} + 3\,H_2O.$$

This reaction is analogous to the action of the halogens and of phosphorus upon hydroxides, forming chloride and hypochlorite, phosphide (phosphine) and hypophosphite, etc. (cf. pp. 312 and 366).

2. By boiling sulfites with sulfur:

$$SO_3^{--} + S \rightarrow S_2O_3^{--}.$$

3. By treating alkali polysulfides with alkali sulfite in the cold:

$$Na_2S_5 + 4\,Na_2SO_3 = 4\,Na_2S_2O_3 + Na_2S.$$

4. By the oxidation of polysulfides:

$$2\,Na_2S_2 + 3\,O_2 = 2\,Na_2S_2O_3.$$

This last reaction takes place on boiling the solution of polysulfide in the air, or very slowly on standing. Yellow ammonium polysulfide is changed, on standing in the air, into ammonium thiosulfate with deposition of sulfur.

The sulfites can be kept well in aqueous solutions, provided they are not subjected to the action of carbon dioxide. They are gradually decomposed by the latter, with separation of sulfur.

The most important commercial thiosulfate is the sodium salt $Na_2S_2O_3 \cdot 5\,H_2O$, the well-known "hypo" of photographers.

Solubility. — The thiosulfates of the alkalies are readily soluble in water, the remaining ones are difficultly soluble; many of them dissolve in an excess of sodium thiosulfate, forming complex ions. The

thiosulfates of the metals of the silver and copper groups are decomposed, as a rule, into insoluble sulfide by contact with boiling water so that sodium thiosulfate can replace hydrogen sulfide as a precipitant in many cases. In this respect, however, it is not so efficient as ammonium thioacetate.

Reactions in the Wet Way

Use a solution of sodium thiosulfate for these reactions.

1. **Sulfuric Acid.** — Both dilute and concentrated sulfuric acid decompose thiosulfates, with deposition of sulfur.

2. **Silver Nitrate** produces a white precipitate, which rapidly becomes yellow, brown, and finally black, owing to the formation of silver sulfide:

$$S_2O_3^{--} + 2\,Ag^+ \rightarrow Ag_2S_2O_3;$$

$$Ag_2S_2O_3 + H_2O = H_2SO_4 + Ag_2S.$$

Silver thiosulfate is soluble in an excess of the reagent. Difficultly soluble $Na[AgS_2O_3]$ is at first formed,

$$Ag_2S_2O_3 + S_2O_3^{--} \rightarrow 2\,[AgS_2O_3]^-,$$

which combines with more thiosulfate, forming a soluble complex salt:

$$2\,[AgS_2O_3]^- + S_2O_3^{--} \rightarrow [Ag_2(S_2O_3)_3]^{---}.$$

But by boiling the dilute solution, silver sulfide is precipitated:

$$[Ag_2(S_2O_3)_3]^{---} \rightarrow S_2O_3^{--} + SO_4^{--} + SO_2\uparrow + S + Ag_2S.$$

Many other metals behave like silver, especially those of the hydrogen sulfide group. Thus copper, mercurous, and tin salts are precipitated as sulfides by boiling the acid solutions with sodium thiosulfate.*

3. **Barium Chloride** in excess produces a white, crystalline precipitate of barium thiosulfate,† difficultly soluble in cold water (500 cc. of water at 18° dissolve about 1 gm. of BaS_2O_3), but fairly soluble in hot water.

4. **Strontium Chloride** produces a white, crystalline precipitate, but only in very concentrated solutions (3.7 cc. of water at 18° dissolve 1 gm. of SrS_2O_3).

5. **Lead Acetate** precipitates white lead thiosulfate, soluble in an excess of the alkali thiosulfate. On boiling the solution a voluminous precipitate, consisting of lead sulfate and lead sulfide, is formed.

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* *Z. anorg. Chem.*, **28**, 223 (1902).

† Rubbing the inside walls of the test-tube hastens the formation of this precipitate.

6. **Iodine Solution** is decolorized by a thiosulfate solution:

$$2\,S_2O_3^{--} + I_2 \rightarrow 2\,I^- + S_4O_6^{--}.$$

The iodine is reduced to iodine anions and the thiosulfate ion is oxidized to tetrathionate ion.

Chlorine and bromine in excess (cf. p. 325) act quite differently upon thiosulfates. If chlorine (or bromine) is conducted into a solution of sodium thiosulfate, a considerable precipitation of sulfur takes place, which, upon further action of the halogen, disappears:

$$S_2O_3^{--} + H_2O + Cl_2 \rightarrow 2\,Cl^- + 2\,H^+ + SO_4^{--} + \mathbf{S};$$

$$\mathbf{S} + 4\,H_2O + 3\,Cl_2 = 8\,H^+ + 6\,Cl^- + SO_4^{--}.$$

7. **Permanganate** is at once decolorized by an acid solution of thiosulfate. The complete oxidation of the thiosulfate corresponds to the formation of sulfate:

$$8\,MnO_4^- + 5\,S_2O_3^{--} + 14\,H^+ \rightarrow 8\,Mn^{++} + 10\,SO_4^{--} + 7\,H_2O.$$

8. **Potassium Chromate** in acid solution is at once reduced to chromic salt:

$$8\,CrO_4^{--} + 3\,S_2O_3^{--} + 34\,H^+ \rightarrow 8\,Cr^{+++} + 6\,SO_4^{--} + 17\,H_2O.$$

In neutral solution a brown precipitate of chromic hydroxide and sulfur is obtained:

$$2\,CrO_4^{--} + 3\,S_2O_3^{--} + 5\,H_2O \rightarrow 3\,SO_4^{--} + 4\,OH^- + 3\,\mathbf{S} + 2\,\mathbf{Cr(OH)_3}.$$

9. **Ferric Chloride** produces, in solutions of sodium thiosulfate, at first a dark-violet coloration (perhaps ferric thiosulfate), which disappears after some time, leaving a colorless solution containing ferrous chloride and sodium tetrathionate:

$$2\,S_2O_3^{--} + 2\,Fe^{+++} \rightarrow 2\,Fe^{++} + S_4O_6^{--}.$$

Similarly,

10. **Cupric Salts** are reduced to colorless cuprous compounds, with the formation of sodium tetrathionate:

$$2\,S_2O_3^{--} + 2\,Cu^{++} \rightarrow Cu_2^{++} + S_4O_6^{--}.$$

The unstable cuprous sulfate immediately acts upon more thiosulfate, forming sodium cuprous thiosulfate:

$$Cu_2^{++} + 2\,S_2O_3^{--} \rightarrow [Cu_2(S_2O_3)_2]^{--}.$$

If the colorless solution of the cuprous salt is treated with caustic potash solution, yellow cuprous hydroxide is in some cases formed immediately, in other cases only on standing or on warming. The precipitate becomes darker colored on being boiled.

If the solution is acidified and boiled, black cuprous sulfide is precipitated.

The colorless solution of the cuprous salt also gives with potassium ferrocyanide a white (usually a light pink) precipitate of cuprous ferrocyanide.

11. **Zinc,** in acid solution, causes the evolution of hydrogen sulfide and formation of some hydrosulfurous acid, $H_2S_2O_4$, in solution:

$$3\,Zn + 2\,H_2S_2O_3 + 6\,H^+ \rightarrow 3\,Zn^{++} + H_2S_2O_4 + 2\,H_2O + 2\,H_2S\uparrow.$$

12. **Zinc Salts** produce no precipitate (difference from sulfides).

13. **Zinc Sulfate and Sodium Nitroprusside** produce no red coloration (difference from sulfites).

14. **Potassium Cyanide.** — Boiling a solution of a thiosulfate with potassium cyanide and caustic soda transforms the thiosulfate into sulfite and the cyanide into thiocyanate:

$$S_2O_3^{--} + CN^- \rightarrow SO_3^{--} + CNS^-.$$

On acidifying the solution with hydrochloric acid and adding ferric chloride, the blood-red color of ferric thiocyanate is obtained (difference from sulfites).

15. **Sodium Nitroprusside** which has been exposed in aqueous solution to air and sunlight until the solution is brown, or which has been treated with one or two drops of potassium ferricyanide solution and a like quantity of sodium hydroxide, gives a deep blue coloration and on standing, heating, or adding a little potassium ferricyanide the color is intensified (difference from Sulfites and Tetrathionates).

16. **Ammonium Molybdate,** in 10 per cent solution, mixed with an equal volume of thiosulfate solution and poured upon some concentrated sulfuric acid in a test-tube, gives a blue ring at the contact zone.

Detection of Sulfurous and Thiosulfuric Acids in the Presence of Hydrogen Sulfide

A Method of E. Votoček.* — *Principle.* — Alkali sulfites, sulfides and polysulfides in slightly alkaline solution will decolorize fuchsin, malachite green or a mixture of these two dyestuffs. If a solution of acetaldehyde or of formalin is added to the decolorized solution, the color returns. Sulfhydrates, thiosulfates and thionates do not decolorize a solution of the above dyestuffs.

Reagent. — Dissolve 0.025 gm. of fuchsin and 0.025 gm. of malachite green separately in 100 cc. portions of water. Mix three volumes of the fuchsin solution with one volume of the malachite green solution.

Procedure. — It is assumed that the solution is slightly alkaline. Test the solution first for sulfide (monosulfide, sulfhydrate and polysulfide) by treating a little of it with 2 or 3 drops of sodium nitroprusside solution. A reddish-violet color shows the presence of the sulfide anion. If sulfide is present, treat the remainder of the solution with cadmium carbonate, shake vigorously, and allow the cadmium sulfide to settle somewhat. Filter and test a new portion of the filtrate with sodium nitroprusside to see if all of the sulfide has been removed. When the sulfide has been removed or proved absent, treat the remainder of the filtrate with a drop of phenolphthalein solution and introduce carbon dioxide gas until the solution is

* *Ber.*, **40**, 414 (1907).

decolorized by it. Take 2 or 3 cc. of this colorless solution and test it with 2 or 3 drops of the fuchsin-malachite-green reagent. If the solution of the dyestuffs is decolorized, a sulfite is present. To the remainder of the solution add a little dilute hydrochloric acid, boil a few minutes, and notice whether there is any deposition of sulfur. If the solution remains clear, no thiosulfate is present.

This is the best method for detecting a sulfide, a sulfite and a thiosulfate in the presence of one another.

(*b*) **Method of Autenrieth and Windaus.*** — The three acids are assumed to be present together in solution in the form of their alkali salts. Treat the fairly concentrated solution with cadmium carbonate, shake and filter off the excess cadmium carbonate and any cadmium sulfide which will be formed if a sulfide is present. Treat the filtrate with strontium nitrate solution and allow it to stand overnight. Filter off any strontium sulfite that may be formed and wash it with a little cold water. If the strontium sulfite is treated on the filter with dilute hydrochloric acid, sulfurous acid goes into solution, which can be detected by its property of decolorizing an iodine solution. In the filtrate from the strontium sulfite, the thiosulfate remains; it can be detected by acidifying with hydrochloric acid and warming, when sulfur will be deposited.

Solubility of Sulfites and Thiosulfates of the Alkaline Earths in Water

	Sulfite	Thiosulfate
Calcium	1 : 800	1 : 2
Strontium	1 : 30,000	1 : 3.7
Barium	1 : 46,000	1 : 480

Reactions in the Dry Way

The thiosulfites of the alkalies, on being heated out of contact with the air, are changed into sulfate and polysulfide, and the latter into sulfide and sulfur:

$$4\,Na_2S_2O_3 \rightarrow 3\,Na_2SO_4 + Na_2S_5,$$

$$Na_2S_5 \rightarrow Na_2S + 4\,S.$$

If this reaction is performed in a closed tube, a sublimate of sulfur is obtained (difference from sulfites); and the residue yields hydrogen sulfide if treated with acid.

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* *Z. anal. chem.*, **1898**, 295. For another method of detecting sulfite in the presence of thiosulfate, cf. F. E. Weston, *Chem. Zentr.*, **1910**, I, 379.

Silver Nitrate produces no precipitate in acid or neutral solutions. **Barium Chloride,** also, causes no precipitation.

NITRIC ACID, HNO_3

Occurrence. — Nitric acid is found in the form of nitrates in small amounts almost everywhere in nature; thus the ammonium salt is found in the atmosphere and in soils; the calcium salt is found in old masonry; while the sodium salt is found in rainless localities, particularly in Chili (Chili saltpetre).

Nitric acid is the final product of the oxidation of ammonia; it is found wherever nitrogenous organic substances have been subjected to decay, forming ammonia. With the help of microörganisms (*Monas nitrificans*, according to Winogradsky) the ammonia is changed first to nitrous acid,

$$2\,NH_3 + 3\,O_2 = 2\,H_2O + 2\,HNO_2,$$

and by further oxidation to nitric acid:

$$2\,HNO_2 + O_2 = 2\,HNO_3.$$

Properties. — Pure nitric acid is a colorless liquid, with a specific gravity of 1.54 at 20°. At 86° it begins to boil, with decomposition, giving off its anhydride, which suffers further decomposition into nitrogen peroxide, NO_2 (brown fumes), and oxygen. By the constant loss of N_2O_5, the nitric acid becomes more and more dilute and the boiling-point constantly rises, until at 120.5° C. it remains constant; when nitric acid of specific gravity 1.414 distills over, forming a 68 per cent acid. If a more dilute acid is subjected to distillation, water is at first given off, the boiling-point constantly rising until 120.5° C. is reached, when a 68 per cent acid again distills unchanged.

Red, *fuming nitric acid* is obtained by conducting NO_2 into the colorless, concentrated acid. In its most concentrated condition it possesses a specific gravity of 1.55.

If the fuming acid is treated with water, it is colored green, and vapors of nitric oxide are given off, which are colored brown on coming in contact with the air. The dissolved NO_2 (or, better, N_2O_4), being a mixed anhydride, is changed into nitric and nitrous acids,

$$N_2O_4 + H_2O \rightarrow HNO_3 + HNO_2,$$

and the nitrous acid, owing to the heat of reaction, is partly changed into nitric acid, with evolution of nitric oxide,

$$3\,HNO_2 = H_2O + HNO_3 + 2\,NO\uparrow,$$

and

$$2\,NO + O_2 = 2\,NO_2\uparrow \text{ (brown vapors)}.$$

Nitric acid is a strong oxidizing agent (cf. p. 31). It is monobasic, and, like the halogen acids, is one of the strongest acids (cf. p. 10). It forms stable salts, which are all soluble in water; but a few of them are changed by water into basic salts (cf. bismuth and mercuric salts), insoluble in water, but soluble in dilute nitric acid.

Reactions in the Wet Way

As nitric acid does not form characteristic insoluble salts, it cannot be detected by means of precipitation; its identification depends upon its oxidizing action. Great care must be exercised before deciding whether this acid is present, for other oxidizing substances give similar (in some cases the same) reactions.

1. **Dilute Sulfuric Acid** gives no reaction (difference from nitrous acid).
2. **Concentrated Sulfuric Acid** when heated with any nitrate causes evolution of yellowish-brown vapors of NO_2, with a characteristic penetrating odor.
3. **Silver Nitrate** and **Barium Chloride** cause no precipitation.
4. **Ferrous Salts** are oxidized by nitric acid, which is itself reduced to nitric oxide, NO.

If the reaction takes place in the cold, the latter combines with the excess of ferrous salt, forming a dark-brown, very unstable compound, e.g. $FeSO_4 \cdot XNO$. This compound is decomposed, on warming, into ferrous salt and nitric oxide (which escapes) the brown color disappearing. If the amount of nitric acid present is more than sufficient to oxidize completely the ferrous salt to ferric salt, a more reddish coloration is obtained owing to the formation of a salt such as $Fe_2(SO_4)_3 \cdot 4\,NO$.

The oxidation of the ferrous salt takes place according to the following reaction,

$$3\,Fe^{++} + NO_3^- + 4\,H^+ \rightarrow 3\,Fe^{+++} + 2\,H_2O + NO\uparrow.$$

The test is best carried out in the following manner:

Place some of the substance to be tested for nitrate in a test-tube with 5 cc. of water, add an equal volume of concentrated sulfuric acid and cool nearly to room temperature by shaking the solution under running water. Carefully add about 5 cc. of saturated ferrous sulfate solution down the sides of the test-tube so that it forms a layer on top of the concentrated sulfuric acid solution. When a nitrate is present a brown ring is formed at the zone of contact between the ferrous sulfate solution and the heavier sulfuric acid solution, or if considerable nitric acid is present the whole of the ferrous sulfate solution may be colored. If only a little nitric acid is present, the zone may be colored pink owing to the formation of $Fe_2(SO_4)_3 \cdot 4\,NO$. The test is not reliable in the presence of an iodide or a chromate.

Nitrous acid gives the same reaction, with the difference that it takes place even without the addition of concentrated sulfuric acid.

5. **Indigo Solution** is decolorized by warming with nitric acid (as well as by other oxidizing agents).

6. **Potassium Iodide** is not decomposed by pure, dilute nitric acid (difference from nitrous acid).

If to the solution of a nitrate, some potassium iodide, a few drops of an acid (best acetic acid), and a little zinc are added, the nitric acid is reduced to nitrous acid, which then reacts with hydriodic acid and the solution becomes yellow on account of the liberation of iodine. By shaking the solution with carbon disulfide, the latter will be colored reddish violet, or the iodine may be detected by adding a little starch paste.

The reactions which take place may be represented by the following equations:

$$Zn + NO_3^- + 2\,H^+ \rightarrow Zn^{++} + NO_2^- + H_2O;$$

$$2\,NO_2^- + 2\,I^- + 4\,H^+ \rightarrow 2\,NO\uparrow + 2\,H_2O + I_2.$$

If it is desired to detect the free iodine by forming a solution in carbon disulfide, the latter *under no circumstances* should be added before the zinc has been allowed to act upon the acid solution of the nitrate and potassium iodide. In such a case, there will often be no separation of iodine, because zinc reduces the carbon disulfide to thioformaldehyde and hydrogen sulfide, and the latter reacts with any iodine which may be formed, changing it back to hydriodic acid:

$$CS_2 + 4\,H^+ + 2\,Zn = 2\,Zn^{++} + CH_2S + H_2S;$$

$$H_2S + I_2 = 2\,HI + S.$$

7. **Diphenylamine Reaction** (the Lunge test *). — *Reagent.* — Dissolve 0.5 gm. of diphenylamine in 100 cc. of pure, concentrated sulfuric acid diluted with 20 cc. of water.

Procedure. — Place a few cubic centimeters of the diphenylamine solution in a test-tube and carefully cover it with the solution to be tested for nitric acid. If the latter is present, there is formed at the zone of contact between the two liquids a ring of a beautiful blue color.

This very sensitive reaction is, unfortunately, also caused by nitrous, chloric, and selenic acids, ferric chloride, and many other oxidizing agents. Even fuming sulfuric acid will give it sometimes.

In the absence of ferric and selenic salts, it is useful for detecting the presence of small amounts of nitrogen acids in sulfuric acid. In this case first pour the concentrated sulfuric acid to be tested into the test-tube and cover it with the specifically lighter diphenylamine solution. If 1 cc. of an acid containing only $\frac{1}{20}$ milligram of nitrogen in a liter is used, the reaction will cause a noticeable coloration. If very strong fuming sulfuric acid is to be tested, dilute it first with concentrated sulfuric acid until it does not contain more than 20 per cent excess SO_3.

8. **Brucine Reaction.** — *Reagent.* — Dissolve 0.2 gm. of brucine in 100 cc. of pure concentrated sulfuric acid.†

* LUNGE, *Z. angew. Chemie*, **1894**, 345.

† LUNGE, *Z. angew. Chemie*, **1894**, 348.

Procedure. — Mix the solution to be tested for nitric acid with three times its volume of pure, concentrated sulfuric acid, and add 1 cc. of brucine solution. If nitric acid is present, a red coloration quickly appears, which quickly changes to orange, then slowly to lemon or gold yellow, and finally becomes greenish yellow. Nitrous acid does not give this reaction provided it is present as "nitrose," i.e., dissolved in concentrated sulfuric acid. Aqueous solutions of nitrites always yield a small amount of nitric acid when acidified with sulfuric acid, and consequently give the brucine reaction.

9. **Zinc in Alkaline Solution** reduces nitric acid to ammonia.

If a nitrate solution is boiled with zinc dust and an alkali, a considerable evolution of ammonia takes place:

$$NO_3^- + 4\,Zn + 7\,OH^- \rightarrow 4\,ZnO_2^{--} + 2\,H_2O + NH_3\uparrow.$$

Aluminium and Devarda's alloy react much more quickly with a drop of caustic soda. This reaction is particularly suited for the detection of nitric acid in the presence of chloric acid (cf. p. 425).

10. **Manganous Chloride.** — A saturated solution of manganous chloride in concentrated hydrochloric acid gives a dark brownish black coloration with a nitrate owing to the formation of $MnCl_3$ in the solution. The reaction is caused by other oxidizing agents.

11. **Salicylic Acid** (2 g. in 30 cc. of concentrated sulfuric acid) gives a yellow coloration when heated with a solid nitrate, nitro-salicylic acid being formed.

12. **Nitron Reaction.** — Nitron (3-n-diphenyl-1,4-endanilo-3,4,dihydro-2,3-triazole) as 10 per cent solution in acetic acid gives a white precipitate of nitron nitrate. The reaction is not characteristic of nitrate ions, as the bromide, iodide, nitrite, chromate, chlorate-perchlorate, thiosulfide, ferrocyanide, ferricyanide and picrate of nitron are insoluble compounds.

Detection of Nitric Acid in the Presence of Nitrous Acid

With the exception of the Lunge-Lwoff* method, there is no absolutely reliable qualitative test for the detection of traces of nitric acid in the presence of large amounts of nitrous acid in aqueous solution. A number of methods have been proposed which depend upon the destruction of the nitrous acid by diazotizing, but they all yield only approximate results; because, in order to destroy the nitrous acid, it is necessary first to set the acid itself free by the addition of another acid, which always causes a part of the nitrous acid to be changed to nitric acid; so that the latter will be detected even when no nitric acid was originally present.

Large amounts of nitric acid in the presence of nitrous acid may be detected by the method proposed by Piccini,† in which a concentrated solution containing salts of both acids is treated with a concentrated solution of urea, and then covered

* This is the colorimetric method described on page 352 and credited to Peter Griess. Lunge-Lwoff modified the procedure.

† *Z. anal. Chem.*, **19**, 354.

(by means of a pipette) with dilute sulfuric acid. A lively evolution of nitrogen and carbon dioxide ensues, which ceases in a few minutes:

$$\underset{\text{Urea}}{CO(NH_2)_2} + 2\,HNO_2 = CO_2\uparrow + 3\,H_2O + 2\,N_2\uparrow.$$

When the evolution of gas has ceased, test the solution for nitric acid by means of the diphenylamine reaction.

This reaction, however, does not take place quickly enough to prevent traces of nitric acid being formed according to the following equation:

$$3\,HNO_2 = H_2O + HNO_3 + 2\,NO\uparrow.$$

The odor of nitrous fumes is always perceptible in the escaping nitrogen,* which can also usually be detected by means of iodo-starch paper. The nitric acid which remains in the solution can be detected by means of the diphenylamine reaction.

The nitrous acid may also be destroyed by boiling an alkaline nitrite solution with neutral ammonium chloride; but traces of nitric acid are always in evidence at the same time.†

If the diphenylamine reaction gives a very intense coloration after the destruction of the nitrous acid by means of urea, the presence of nitric acid in the original compound is assured; but if the reaction shows that only a trace of nitric acid is present it is probably due simply to small amounts of nitric acid formed by the destruction of the nitrous acid.

Reactions in the Dry Way

By the ignition of nitrates of the alkalies, they are changed into nitrites with loss of oxygen, and the latter are decomposed on stronger ignition into oxide:

$$2\,KNO_3 = 2\,KNO_2 + O_2\uparrow,$$
$$4\,KNO_2 = 2\,K_2O + 4\,NO\uparrow + O_2\uparrow.$$

All nitrates deflagrate on being heated on charcoal; i.e., the charcoal burns at the expense of the oxygen of the nitric acid, with vivid scintillation.

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* Even at 0° and in an atmosphere of carbon dioxide.

† By evaporating with ammonium carbonate solution the decomposition scarcely takes place at all.

CHLORIC ACID, $HClO_3$

Free chloric acid is extremely unstable, and is decomposed at 40°, into perchloric acid with loss of chlorine and oxygen (cf. p. 179):

$$3\,HClO_3 \rightarrow H_2O + 2\,ClO_2\uparrow + HClO_4,$$

and

$$2\,ClO_2 = Cl_2\uparrow + 2\,O_2\uparrow.$$

The aqueous solution of chloric acid behaves as a strong acid; in 0.5 normal solution it is 88 per cent ionized. The salts of the monobasic chloric acid, the chlorates, are quite stable and are all soluble in water. They are formed by conducting chlorine into hot alkali hydroxide solutions, which are not too concentrated.*

$$6\,OH^- + 3\,Cl_2 \rightarrow 5\,Cl^- + ClO_3^- + 3\,H_2O.$$

Reactions in the Wet Way

1. **Dilute Sulfuric Acid** sets free chloric acid from chlorates, which, as above stated, is gradually decomposed, with loss of chlorine and oxygen, into perchloric acid. The solution, therefore, acts as an oxidizing agent, particularly on warming; it will turn iodo starch blue:

$$ClO_3^- + 6\,I^- + 6\,H^+ \rightarrow Cl^- + 3\,H_2O + 3\,I_2.$$

The speed of the reaction between the chlorate and the iodide depends upon the concentration of the hydrogen ion. The neutral salts do not act as oxidizing agents (difference from hypochlorites).

Test for Hypochlorite in Chlorates

To test for the presence of hypochlorite in an alkali chlorate, dissolve about 2 gm. of the salt in 200 cc. of water, add 3 cc. of 10 per cent KI solution and 3 cc. of starch solution, but *no sulfuric acid;* the solution will at once turn blue if a trace of hypochlorite is present. As little as 0.1 mgm. of hypochlorite will give the test.

2. **Concentrated Sulfuric Acid** decomposes all chlorates, setting free greenish-yellow chlorine dioxide gas, which colors the sulfuric acid yellow and explodes violently on warming:

$$3\,KClO_3 + 3\,H_2SO_4 = 3\,KHSO_4 + HClO_4 + 2\,ClO_2\uparrow + H_2O.$$

A very small crystal of chlorate added to 1 cc. of concentrated sulfuric acid on a watch glass will color the acid and give a chlorine-like odor.

* F. WINTELER, *Z. anorg. Chem.*, **33**, 188 (1902).

3. **Silver Nitrate** and **Barium Chloride** do not cause precipitation.

4. **Reducing Agents** reduce chlorates to chlorides in acid, alkaline, and neutral solutions.

The reduction in acid solution is effected by means of zinc and dilute sulfuric acid, sulfurous acid, or sodium nitrite:

$$3\,Zn + ClO_3^- + 6\,H^+ \rightarrow 3\,Zn^{++} + Cl^- + 3\,H_2O;$$
$$3\,SO_3^{--} + ClO_3^- \rightarrow Cl^- + 3\,SO_4^{--}.$$
$$3\,NO_2^- + ClO_3^- \rightarrow 3\,NO_3^- + Cl^-.$$

The reduction in alkaline or neutral * solution is brought about by boiling the solution with zinc dust, aluminium powder, by means of Devarda's alloy (cf. p. 35), or by a copper-zinc couple †):

$$ClO_3^- + 3\,Zn + 6\,OH^- \rightarrow 3\,ZnO_2^{--} + Cl^- + 3\,H_2O.$$

The residual metal is filtered off, the solution acidified with nitric acid,‡ and silver nitrate added, when the characteristic, curdy precipitate of silver chloride is formed.

5. **Concentrated Hydrochloric Acid** decomposes all chlorates; the acid is colored yellow and chlorine is evolved:

$$ClO_3^- + 5\,Cl^- + 6\,H^+ \rightarrow 3\,H_2O + 3\,Cl_2\uparrow.$$

This equation is not quite correct, for some ClO_2 is always mixed with the Cl_2. The following equation expresses this:

$$3\,ClO_3^- + 7\,Cl^- + 10\,H^+ \rightarrow 5\,H_2O + 4\,Cl_2\uparrow + 2\,ClO_2\uparrow.$$

The proportion of ClO_2 and Cl_2 formed is influenced by the concentration of the reacting substances and the temperature.

If the hydrochloric acid was colored blue with indigo it will be decolorized by the free chlorine.

6. **Ferrous Salts.** — By boiling chlorates with ferrous salts in the presence of dilute acid, the chlorate is quickly reduced to chloride (difference from perchloric acid):

$$ClO_3^- + 6\,Fe^{++} + 6\,H^+ \rightarrow 3\,H_2O + Cl^- + 6\,Fe^{+++}.$$

7. **Diphenylamine** reacts the same as with nitric acid.

8. **Indigo Test.** — To the chlorate solution add enough indigo, dissolved in concentrated sulfuric acid, to give a light blue color. Add a little dilute sulfuric acid and introduce drop by drop a little sulfurous acid or sodium sulfite solution. The blue color will disappear quickly. The sulfurous acid reacts with the chlorate to form chlorine or hypochlorite and the chlorine or hypochlorite oxidizes the indigo. The test is sensitive.

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* The reaction takes place very slowly in neutral solutions.

† Treat granulated zinc with one per cent copper sulfate solution, wash and dry the residue.

‡ On acidifying with nitric acid a heavy precipitate of $Zn(OH)_2$ is obtained which dissolves in more nitric acid.

9. **Aniline Sulfate Test.** — Add a little of the solid to be tested to about 1 cc. of concentrated sulfuric acid and introduce one or two drops of an aqueous aniline sulfate solution; a deep blue color is obtained with a chlorate but not with a nitrate.

Detection of Hydrochloric, Nitric, and Chloric Acids in the Presence of One Another

I. First, test for the presence of chloride anions by treating a part of the solution with silver nitrate; a white precipitate of silver chloride shows the presence of hydrochloric acid. Treat the remainder of the solution with silver sulfate solution until no further precipitation of silver chloride takes place, and filter off the precipitate.

Boil the filtrate with a little caustic potash (in order to expel any ammonia from ammonium salts which may be present), add zinc dust (or Devarda's alloy), and again boil; if nitric acid is present, ammonia will be given off. Filter off the residue, acidify the filtrate with nitric acid and treat with silver nitrate. If a precipitate of silver chloride is now obtained, chloric acid was originally present.

II. Or, test a small part of the solution for hydrochloric acid by adding silver nitrate in excess, filter off the precipitate, treat the filtrate with sulfurous acid, and again test with silver nitrate: a precipitate of silver chloride shows the presence of chloric acid. Enough nitric acid must be added to dissolve any silver sulfite that may form.

Test a second portion of the solution, as above, for nitric acid.

Reactions in the Dry Way

On ignition, all chlorates are decomposed, forming a chloride with loss of oxygen. By heating on charcoal, deflagration takes place.

PERCHLORIC ACID, $HClO_4$

Free perchloric acid is obtained by the distillation of potassium perchlorate with concentrated sulfuric acid. In this way the solid, crystalline hydrate $HClO_4 + H_2O$ is obtained, and, on heating to 110°, the anhydrous liquid acid distills off first and fumes strongly in the air, while the oily hydrate $HClO_4 + 2\ H_2O$ remains behind until the temperature reaches 203° C., when it also distills.

The concentrated acid is very dangerous, and often explodes when in contact with bits of charcoal, wood, paper or dust. In aqueous solution, however, it can be kept without danger and contains mostly the ionized acid.

The salts of this monobasic acid, the perchlorates, are remarkably stable; they contain chlorine with seven positive charges and are isomorphous with the permanganates. The potassium salt is obtained from potassium chlorate. On melting the latter compound, at first a lively stream of oxygen is given off which, however, soon lessens. The melt quickly becomes viscous, and consists of potassium chloride and potassium perchlorate,

$$2\ KClO_3 = KCl + KClO_4 + O_2\uparrow,$$

and the latter may be separated from the much more soluble potassium chloride by recrystallization.

Solubility. — All perchlorates are soluble in water.

Reactions in the Wet Way

Perchloric acid is not attacked by concentrated sulfuric acid, nor reduced to chloride by zinc dust, Devarda's alloy, sulfurous acid, or acid solutions of ferrous salts.

1. **Potassium Salts** precipitate the relatively-insoluble, white, crystalline $KClO_4$ (cf. p. 85) insoluble in alcohol. Ammonium salts give a similar precipitate.

2. **Silver Nitrate** and **Barium Chloride** produce no precipitation.

3. **Titanium Trichloride,** $TiCl_3$, hydrosulfurous acid, $H_2S_2O_4$, and the lower oxidation products of vanadium, molybdenum and tungsten reduce perchlorates to chlorides.

Reactions in the Dry Way

The perchlorates deflagrate on being heated on charcoal; on fusing they lose oxygen, leaving chloride behind, which when dissolved in

water gives all the reactions for hydrochloric acid. If a perchlorate is fused with a chloride, e.g. zinc chloride, chlorine is evolved. If the chlorine is driven over, by a stream of carbon dioxide, into potassium iodide solution, iodine is set free. If nitrates are present, they can be decomposed first by evaporating to dryness with concentrated hydrochloric acid, and then to make sure that no traces of nitrate remain, Gooch and Kreider recommend evaporating with manganous chloride and concentrated hydrochloric acid, and again evaporating with hydrochloric acid. Finally they precipitate the manganese with sodium carbonate, filter and evaporate the filtrate to dryness and then test the residue for chlorate by fusing with zinc chloride.

PERSULFURIC ACID, $H_2S_2O_8$

Pure persulfuric acid itself has never been isolated, its solution in sulfuric acid alone being known. It was first prepared by M. Marshall,* who electrolyzed fairly dilute sulfuric acid, keeping it very cold. During the electrolysis hydrogen ions are discharged at the cathode and unite to form hydrogen molecules, while HSO_4 anions are discharged at the anode and unite to form persulfuric acid:

$$2\,H_2SO_4 \rightarrow H_2 + H_2S_2O_8.$$

The preparation of ammonium persulfate, from which all other persulfates are made, is entirely analogous.

The most important salts of persulfuric acid are those of ammonium, potassium, and barium. $(NH_4)_2S_2O_8$ is readily soluble in water, and forms monoclinic crystals; $K_2S_2O_8$ is difficultly soluble in cold water, but much more soluble in hot water, from which solution it is obtained by rapid cooling in the form of long crystals; $BaS_2O_8 + 4\,H_2O$ is made by rubbing ammonium persulfate with barium hydroxide, and is fairly soluble in water.

Reactions

A solution of ammonium persulfate may be used.

1. **Water.** — All persulfates are decomposed in aqueous solution (slowly in the cold, but more quickly on warming), forming sulfate, free sulfuric acid, and oxygen:

$$2\,S_2O_8^{--} + 2\,H_2O \rightarrow 4\,HSO_4^- + O_2\uparrow,$$

$$2\,BaS_2O_8 + 2\,H_2O \rightarrow 2\,BaSO_4 + 2\,H_2SO_4 + O_2\uparrow.$$

A large proportion of the oxygen escapes as ozone, which can be detected by its odor, or by its property of turning iodo-starch paper blue. A dilute solution of ammonium persulfate decomposes slowly at 20° C., without evolution of oxygen, part of the nitrogen being oxidized to nitric acid:

$$4\,(NH_4)_2S_2O_8 + 3\,H_2O = 7\,(NH_4)HSO_4 + H_2SO_4 + HNO_3.$$

2. **Dilute Sulfuric Acid** acts the same as water.

3. **Concentrated Sulfuric Acid.** — If a solid persulfate is dissolved in concentrated sulfuric acid at 0° C., a liquid is obtained which pos-

* *J. Chem. Soc.*, **59**, 771.

sesses very strong oxidizing properties. The mixture is known as Caro's acid.* For further particles concerning this acid see below.

4. **Silver Nitrate** precipitates black silver peroxide:

$$2\,Ag^+ + S_2O_8^{--} + 2\,H_2O \rightarrow 2\,HSO_4^- + 2\,H^+ + \mathbf{Ag_2O_2}.$$

If, however, the concentrated solution of ammonium persulfate is treated with ammonia and a very little silver nitrate, a lively evolution of nitrogen takes place, and the solution becomes heated to boiling. Silver peroxide is formed first, and oxidizes the ammonia to water, setting free nitrogen (catalysis).†

5. **Manganese, Cobalt, Nickel,** and **Lead Salts** are oxidized in the presence of alkali to black peroxides:

$$Mn^{++} + S_2O_8^{--} + 4\,OH^- \rightarrow 2\,SO_4^{--} + \mathbf{H_2MnO_3} + H_2O.$$

In this last reaction persulfuric acid reacts exactly similarly to hydrogen peroxide. It may be distinguished, however, from the latter by the fact that it does not decolorize a solution of potassium permanganate, does not produce a yellow coloration with titanium sulfate, and does not react with chromic acid to form chromium peroxide (cf. p. 147). Ferrous salts are readily oxidized to ferric salts, and cerous salts are changed to yellow ceric salts by persulfates, but the latter are not decolorized by an excess of the persulfate, while they are by hydrogen peroxide.

Manganese and lead salts are precipitated quantitatively from neutral and slightly acid solutions by alkali persulfates, cobalt incompletely from neutral solutions and not at all from acid ones, and nickel only in the presence of alkali. Hydrogen peroxide produces precipitates of peroxides in all these solutions only in the presence of alkali. In the presence of silver ions, which have a catalytic effect, manganous ions are oxidized to permanganate in hot nitric acid solutions by means of alkali persulfates.

$$5\,S_2O_8^{--} + 2\,Mn^{++} + 8\,H_2O \rightarrow 2\,HMnO_4 + 10\,SO_4^{--} + 14\,H^+.$$

6. **Barium Chloride** does not give a precipitate immediately in a freshly-prepared, cold solution of a persulfate; but, on standing some time, or on boiling, insoluble barium sulfate is precipitated.

7. **Potassium Iodide** reacts with neutral solutions of persulfate and iodine is liberated:

$$2\,I^- + S_2O_8^{--} \rightarrow 2\,SO_4^{--} + I_2.$$

Percarbonates and perborates do not give this reaction.

Monopersulfuric Acid (Caro's Acid) H_2SO_5

This acid is formed by the hydrolysis of persulfuric acid,

$$H_2S_2O_8 + H_2O \rightarrow H_2SO_4 + H_2SO_5,$$

and by the action of perhydrol (30 per cent hydrogen peroxide) on sulfuric acid:

$$H_2SO_4 + H_2O_2 \rightarrow H_2O + H_2SO_5.$$

* *Z. angew. Chem.*, **1898**, 845; *Ber.*, **34**, 853 (1901); *Ber.*, **41**, 1839 (1909).

† *Z. phys. Chem.*, **37**, 255 (1901).

Unlike hydrogen peroxide, it does not reduce permanganates and it causes the liberation of iodine from potassium iodide solutions more readily than persulfates do.

$$H_2SO_5 + 2\,H^+ + 2\,I^- \rightarrow H_2SO_4 + H_2O + I_2.$$

It is usually assumed that hydrogen peroxide, persulfuric acid and monopersulfuric acid all contain an atom of oxygen directly connected to another atom of oxygen; this atom of oxygen, therefore, has a positive and a negative charge residing upon it (cf. p. 33).

Silver Nitrate produces no precipitate.

Barium Chloride produces a white precipitate, insoluble in acids.

SULFURIC ACID, H_2SO_4

Pure sulfuric acid at ordinary temperatures is a colorless, oily liquid of specific gravity 1.838; at low temperatures it is a solid. If the acid is subjected to distillation, it is always partially decomposed; heavy, white vapors of SO_3 are given off first, and at 338° C. a 98 per cent acid distills over. Ordinary commercial sulfuric acid has a specific gravity of 1.83–1.84, and contains 93–96 per cent H_2SO_4. The maximum density is reached when 97.35 per cent H_2SO_4 is present. Commercial sulfuric acid often contains lead sulfate, selenic acid, platinum, palladium, arsenious acid, the nitrogen acids, and small amounts of organic matter (whereby it is often colored brown) as impurities. Concentrated sulfuric acid is very hygroscopic, and is used for drying gases, etc.

The anhydride of sulfuric acid, SO_3, dissolves in concentrated sulfuric acid, forming pyrosulfuric acid, $H_2S_2O_7$, which is solid at ordinary temperatures, melts at 35°, and loses SO_3 at higher temperatures. It fumes strongly, and is called, therefore, *fuming sulfuric acid.* Sulfuric acid is dibasic and forms both neutral and acid salts.

Solubility. — Most sulfates are soluble in water; calcium sulfate is difficultly soluble, strontium and lead sulfates are very difficultly soluble, while barium sulfate is practically insoluble in water. There are also a number of basic sulfates, Hg, Bi, Cr, which are insoluble in water, but are, as a rule, easily dissolved by dilute acid.

Reactions in the Wet Way

1. **Sulfuric Acid** naturally gives no reaction.

2. **Silver Nitrate** causes no precipitation in dilute solutions, but in concentrated solutions a white, crystalline precipitate is formed (100 cc. of water dissolve at 18° C. only 0.58 gm. of silver sulfate).

3. **Barium Chloride** precipitates, from even the most dilute solutions, white barium sulfate, insoluble in acids.

4. **Lead Acetate** precipitates white lead sulfate, soluble in concentrated sulfuric acid, ammonium acetate, and ammonium tartrate solutions (cf. p. 222).

To detect the presence of SO_4 in insoluble sulfates, treat with sodium carbonate, whereby insoluble carbonate and soluble sodium sulfate are formed.

Lead sulfate and calcium sulfate are easily decomposed by *boiling* with sodium carbonate solution, but barium and strontium sulfates are only incompletely decomposed by this treatment; they are much more readily attacked by *fusing* with four times as much sodium carbonate (cf. p. 116).

Even barium sulfate, however, is decomposed sufficiently for the purposes of qualitative analysis by *boiling* with sodium carbonate.

5. **By Metals** in acid solution the sulfates are not reduced.

Reactions in the Dry Way

The neutral salts of the alkalies melt with difficulty without being decomposed, while the acid salts of the alkalies readily give off water and SO_3 (cf. p. 138).

The sulfates of the alkaline earths and of lead do not undergo decomposition on ordinary ignition; the remaining sulfates are more or less decomposed.

All sulfates are reduced to sodium sulfide when heated with sodium carbonate on charcoal; if the product is placed upon a bright silver coin and moistened, a black stain of silver sulfide results, e.g.:

$$(a)\ CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4;$$

$$(b)\ Na_2SO_4 + 2\,C = 2\,CO_2 + Na_2S;$$

$$(c)\ 2\,Na_2S + 4\,Ag + 2\,H_2O + O_2 = 4\,NaOH + 2\,Ag_2S.$$

This reaction is called the Hepar reaction and is obtained with all substances that contain sulfur.

HYDROFLUORIC ACID, H_2F_2 (or HF)

Occurrence. — Hydrofluoric acid occurs in nature only in the form of fluorides, of which the most important is fluorite, CaF_2, crystallizing in the isometric system. It is also found as cryolite, $Na_3[AlF_6]$, in Greenland, and in many silicates, such as tourmaline, topaz, lepidolite, apophyllite, apatite, etc.

Preparation. — Hydrofluoric acid is obtained by decomposing a fluoride with concentrated sulfuric acid in platinum or lead retorts:

$$CaF_2 + H_2SO_4 = CaSO_4 + H_2F_2 \uparrow .$$

Properties. — Hydrofluoric acid at temperatures above 20° C. is a colorless gas which changes at 19.4° C. to a mobile, fuming liquid. The vapors possess a penetrating odor and are poisonous. When in contact with the skin, the acid produces painful burns. On heating the concentrated aqueous solution, the gas H_2F_2 at first distills and then the 36 per cent acid.

Hydrofluoric acid is distinguished from all other acids by its ability to dissolve silicic acid, a property which is utilized technically for etching glass, and in the analytical laboratory for detecting fluorine and silicic acid, as well as for decomposing silicates. On account of this action upon glass the acid must be kept in platinum, wax, or hard rubber, and prepared in platinum or lead vessels.

The action of hydrofluoric acid upon silicic acid takes place according to the equation

$$SiO_2 + 2\,H_2F_2 = 2\,H_2O + SiF_4 \uparrow ,$$

and the velocity of the reaction depends upon the fineness and nature of the material. Thus Mackintosh * found after one hour's action of an excess of 9 per cent hydrofluoric acid upon quartz and opal powder that the quartz had lost only 1.56 per cent of its original weight while the opal had lost 77.28 per cent.

If precipitated and ignited silica is treated with strong hydrofluoric acid, it dissolves almost immediately with hissing and strong evolution of heat, while quartz powder under the same treatment is dissolved only slowly.

Most silicates, with regard to the ease with which they are attacked by hydrofluoric acid, stand intermediate between the precipitated silica and quartz, although some silicates are attacked more difficultly than is quartz, and a few are only slightly acted upon.

Hydrofluoric acid, HF, in dilute aqueous solutions is a weak, monobasic acid having, in common with other weak acids like carbonic acid, acetic acid, etc., the property of turning blue litmus red and Brazil-wood paper yellow. The ionization constant is about 7.2×10^{-4}. In concentrated solutions, hydrofluoride ions are formed,

$$HF + F^- \rightarrow HF^-$$

* *Chem. News*, **54**, 102.

and the primary ionization of the dibasic H_2F_2 is considerably greater than that of the simpler molecules. The aqueous solution of an alkali fluoride has a strong alkaline reaction.

The property of forming very stable complex metal-hydrofluoric acids is characteristic of hydrofluoric acid as of hydrocyanic acid,

$$H[AgF_2],\ H[KF_2],\ H[NaF_2] \text{ and } H[NH_4F_2],$$

and corresponding to ferricyanic acid, $H_3[Fe(CN)_6]$:

$$Na_3[FeF_6],\ Na_3[AlF_6], \text{ etc.}$$

Unlike the complex cyanogen compounds, of which the free acids either do not exist at all or represent very unstable compounds, the corresponding fluorine acids are fairly stable. Thus hydroargentifluoric acid, $H[AgF_2]$ decomposes only on gently heating it, into silver fluoride and hydrofluoric acid, and the corresponding alkali compounds are decomposed only upon ignition; for this reason the latter are suitable for attacking difficultly decomposable silicates, zircon and titantium minerals, etc., which are only partially attacked by free hydrofluoric acid.

Solubility. — The fluorides of the alkalies, of silver, aluminium, tin, and mercury are soluble in water, while those of the alkaline earths, of lead, copper, and zinc, are insoluble, or at least very difficultly soluble.

Reactions in the Wet Way

For reactions 1, 2, and 3, use powdered calcium fluoride, but for reactions 4, 5, 6, and 7, use a solution of sodium fluoride.

1. **Dilute Sulfuric Acid** causes only a slight reaction.

2. **Concentrated Sulfuric Acid** reacts readily on warming, setting free hydrofluoric acid:

$$\mathbf{CaF_2} + H_2SO_4 = \mathbf{CaSO_4} + H_2F_2\uparrow.$$

Acid containing about 90 per cent H_2SO_4 is most suitable for this reaction. Acid containing an excess of SO_3 is likely to cause the formation of difficultly-volatile fluorsulfonic acid, HSO_3F.

If the reaction is performed in a test-tube, the hydrofluoric acid will attack the glass, forming volatile silicon fluoride and salts of hydrofluosilicic acid; but the latter are decomposed by the concentrated sulfuric acid into sulfate, hydrofluoric acid, and silicon fluoride,

$$\underset{\text{Soda glass}}{\mathbf{Na_2CaSi_6O_{14}}} + 14\,H_2F_2 = 14\,H_2O\uparrow + \mathbf{Na_2SiF_6} + \mathbf{CaSiF_6} + 4\,SiF_4\uparrow,$$

and

$$\mathbf{Na_2SiF_6} + H_2SO_4 = \mathbf{Na_2SO_4} + H_2F_2\uparrow + SiF_4\uparrow,$$
$$\mathbf{CaSiF_6} + H_2SO_4 = \mathbf{CaSO_4} + H_2F_2\uparrow + SiF_4\uparrow.$$

The silicon fluoride formed by this reaction is a colorless gas with a penetrating odor, and is decomposed by water, forming gelatinous silicic acid and hydrofluoric acid,

$$(1)\ SiF_4 + 4\,H_2O = \mathbf{H_4SiO_4} + 2\,H_2F_2\uparrow.$$

Silicon fluoride, however, readily combines with hydrofluoric acid to form hydrofluosilicic acid:

$$(2)\ SiF_4 + H_2F_2 = H_2[SiF_6],$$

and the latter compound is not decomposed by water. The entire reaction, therefore, which takes place between silicon tetrafluoride and water is expressed by the sum of the two equations, as follows:

$$3\,SiF_4 + 4\,H_2O = H_4SiO_4 + 2\,H_2[SiF_6].$$

If, therefore, a fluoride be heated in a glass test-tube with concentrated sulfuric acid, and the escaping vapors allowed to act upon water by placing a moist glass rod in the tube, the water adhering to the rod will become turbid.

Remark. — Although the above test rarely fails when relatively large amounts of fluoride are used, it will not be obtained in the case of certain minerals containing fluorine, such as topaz, tourmaline, etc. The test may fail, furthermore, if the fluoride is mixed with a large excess of that modification of silicic acid which is most readily attacked by hydrofluoric acid. According to Daniel,* this is due to the formation of a stable oxyfluoride, probably of the formula $SiOF_2$.

The silicon tetrafluoride at first formed combines with the excess of amorphous silicic acid present, as follows,

$$SiF_4 + SiO_2 = 2\,SiOF_2,$$

but this reaction will take place only very slowly, if at all, with quartz powder or with the silica of a silicate such as glass.

A positive result will be obtained invariably when the tetrafluoride test is made in a platinum vessel with a relatively large amount of fluoride and comparatively little amorphous silicic acid or silicate (large amounts of quartz do not influence the reaction); the test will be negative, on the other hand, if made in platinum with no silicic acid, or, strange to say, when only quartz is present with the fluoride. The reason for this different behavior lies in the difficulty with which quartz is attacked by hydrofluoric acid.

Daniel recommends the following method for performing the test:

Mix the substance to be tested for fluorine with about three times as much (by volume) of ignited quartz powder, place the mixture in a test-tube and stir it into a thin paste with concentrated sulfuric acid. Close the test-tube with a cork in which one hole has been bored and an opening cut in the side. Through the hole in the cork insert a glass rod blackened with asphalt paint, and on the bottom of the rod suspend a drop of water; push this rod down into the tube until it is only a distance equal to about 1½ times the diameter of the test-tube from the paste in the bottom. Gently heat the tube and its contents over a small flame, and if a fluoride is present a white film of H_4SiO_4 will be formed in the drop of water and will be shown plainly in contrast to the black rod. In a tube with 1 cm. diameter, fluorine equivalent to 1 mgm. CaF_2 may be detected, while with a tube of only 0.5 cm. diameter as little as 0.1 mgm. CaF_2 will give the test. When using a tube of small diameter, it is best to add the sulfuric acid through a small capillary pipette to avoid wetting the sides of the tube.

If the substance contains considerable amorphous silica, or when an oxyfluoride, such as topaz, is present, which is hard to decompose with sulfuric acid, the test will fail, and it is then necessary to make use of the etching test.

3. **The Etching Test.** — Place the substance to be tested for fluoride in a platinum crucible, add some concentrated sulfuric acid, and cover the crucible with a watch-glass whose convex side has a thin coating of beeswax through which a few letters have been scratched with a pointed match. On warming the contents of the crucible,

* *Z. anorg. Chem.*, **38** (1904, 299).

the glass will be etched at the places where the escaping gas comes in contact with it, if a fluoride was originally present. By covering the upper concave side of the watch-glass with a little cold water, the wax coating will not melt during the experiment.

If it is desired to detect the presence of a trace of fluorine, allow the crucible to stand covered with the watch-glass for twelve hours and then heat for a few minutes. The presence of only 0.3 mgm. CaF_2 is sufficient to give this test, provided a crucible of the right size is used.

If the fluoride contained silica (as in topaz, tourmaline, and other minerals), the etching test will be negative, for even if the fluorine escapes, it will be in the form of silicon fluoride, which does not attack glass.

To detect small amounts of fluoride in silicates, it is necessary first to transform the fluorine into calcium fluoride and to subject the latter compound to the test.

To obtain the fluorine as calcium fluoride, proceed as follows:

Fuse the finely-pulverized silicate with six to eight times as much sodium carbonate in a platinum crucible, and treat the melt with water after it is cold. A solution is thus obtained in which all of the fluorine is present as sodium fluoride, together with sodium silicate. Precipitate the silicic acid by adding considerable ammonium carbonate to the solution, warming it slightly, and allowing it to stand twelve hours. After filtering off the silica, evaporate the solution to a small volume, and add a little phenolphthalein, which will impart a pink color to the solution on account of its being slightly alkaline. Carefully add hydrochloric acid until the stirred solution becomes colorless, and heat to boiling, when the color will reappear. Again decolorize the solution with hydrochloric acid after it has become cold, and repeat the process until the solution becomes only faintly colored on boiling it.

Now add calcium chloride solution and again boil the solution. The precipitate consists of calcium carbonate and calcium fluoride; filter it off, wash, dry, and ignite it in a platinum crucible. Treat the ash with dilute acetic acid, evaporate to dryness, triturate with water and filter off the undissolved calcium fluoride. After drying the precipitate and burning the filter, it is ready for the etching test.

4. **Silver Nitrate** causes no precipitation from solutions of soluble fluorides.

5. **Barium Acetate** precipitates barium fluoride soluble in an excess of mineral acid and in ammonium salts. Traces of fluorine present as preservative in foods, liquors, etc., may be detected by adding a little potassium sulfate (about 0.3 gm.) to the solution, heating it to boiling and slowly introducing 10 cc. of 10 per cent barium acetate solution. The precipitate of barium sulfate and fluoride is then subjected to the etching test.*

6. **Calcium Chloride** gives a white, slimy precipitate, difficultly soluble in hydrochloric and nitric acids, but almost entirely insoluble in acetic acid. On account of its slimy consistency, the precipitated calcium fluoride is extremely hard to filter; but by precipitating it in the presence of calcium carbonate a mixture is obtained which

* Cf. BLAREZ, *Chem. News*, **91**, 39; also WOODMAN and TALBOT, *J. Am. Chem. Soc.*, **27**, 1437.

can be readily filtered. After igniting and treating with acetic acid, the precipitate is changed to soluble calcium acetate and insoluble calcium fluoride; it is now much denser and can be filtered readily.

7. **Ferric Chloride** produces in concentrated solutions of alkali fluorides a white, crystalline precipitate corresponding to the general formula $M_3[FeF_6]$. These salts, which are analogous to cryolite, $Na_3[AlF_6]$, are difficultly soluble in water, and their saturated, aqueous solutions do not give the iron reaction upon the addition of potassium thiocyanate, except after the addition of acid. These complex fluorides also are slightly decomposed by ammonia, forming a basic ferric fluoride.

Methods for Getting Insoluble Fluorides into Solution

(*a*) Calcium fluoride alone cannot be decomposed completely by fusing with sodium carbonate. The aqueous solution of the melt always contains a considerable amount of sodium fluoride, but never the total amount of the fluorine. If, however, the fluoride is mixed with silica or a silicate, complete decomposition can be effected by fusing with sodium carbonate. The silica decomposes calcium fluoride, forming calcium fluosilicate and calcium silicate, salts which are decomposed by fusion with sodium carbonate.

On treating the melt with water, sodium fluoride and sodium silicate go into solution, while the calcium is left behind on the carbonate, and can be dissolved by treatment with dilute hydrochloric acid. To detect fluorine in silicates, they should first be subjected to sodium carbonate fusion.

(*b*) All fluorides are decomposed by heating with concentrated sulfuric acid, being changed to sulfates.

Reactions in the Dry Way

Most fluorides are unchanged by ignition. By heating them with silica in moist air, they are all more or less completely decomposed:

$$CaF_2 + H_2O + SiO_2 = CaSiO_3 + H_2F_2\uparrow.$$

$$2\,H_2F_2 + SiO_2 = SiF_4\uparrow + 2\,H_2O.$$

The acid fluorides give off hydrofluoric acid on ignition, whereby the glass tube in which they are heated becomes etched.

HYDROFLUOSILICIC ACID, H_2SiF_6

As we have seen, this acid is formed by the action of silicon fluoride upon water:

$$3\,SiF_4 + 4\,H_2O = 2\,H_2[SiF_6] + H_4SiO_4.$$

If the silicic acid is filtered off, a strongly-acid solution is obtained containing hydrofluosilicic acid. By evaporating the solution, the acid is decomposed into silicon fluoride and hydrofluoric acid,

$$H_2[SiF_6] = SiF_4\uparrow + H_2F_2\uparrow,$$

so that hydrofluosilicic acid itself is known only in aqueous solution, although its salts are very stable.

Solubility. — Most fluosilicates are soluble in water; the potassium and barium salts form exceptions, being difficultly soluble in water and insoluble in alcohol.

Reactions in the Wet Way

A solution of sodium fluosilicate should be used.

1. **Dilute Sulfuric Acid** causes only a very slight decomposition.

2. **Concentrated Sulfuric Acid** decomposes fluosilicates, evolving silicon fluoride and hydrofluoric acid:

$$Na_2SiF_6 + H_2SO_4 = Na_2SO_4 + SiF_4\uparrow + H_2F_2\uparrow.$$

If the reaction is performed in a platinum crucible, the escaping gas will etch glass, and will cause a drop of water to become turbid.

3. **Silver Nitrate** produces no precipitation.

4. **Barium Chloride** gives a crystalline precipitate (1 gm. $Ba[SiF_6]$ dissolves in about 3750 cc. of water at 17°).

5. **Potassium Chloride** produces, from solutions which are not too dilute, a gelatinous precipitate of potassium fluosilicate, which is difficultly soluble in water (1 gm. of $K_2[SiF_6]$ dissolves in 835 cc. of water at 17°) and much more insoluble in an excess of potassium chloride or in alcohol, but soluble in ammonium chloride.

6. **Ammonia** decomposes all soluble fluosilicates, with separation of silicic acid:

$$Na_2SiF_6 + 4\,NH_4OH = 2\,NaF + 4\,NH_4F + H_4SiO_4.$$

7. **Potassium** and **Sodium Hydroxides** react in the same way as ammonia, but the silicic acid remains in solution as alkali silicate.

Reactions in the Dry Way

Fluosilicates are decomposed on being heated into fluoride of the metal and silicon fluoride:

$$K_2SiF_6 = 2\,KF + SiF_4\uparrow .$$

The escaping gas renders a drop of water turbid, and the residue gives all the reactions of a fluoride.

GROUP VII

NON-VOLATILE ACIDS WHICH FORM SOLUBLE SALTS WITH THE ALKALIES

SILICIC ACID, H_4SiO_4 AND H_2SiO_3

Occurrence. — The above acids, from which very stable salts are derived, are not known in the free state, as is the case with carbonic and sulfurous acids. There are, however, amorphous, natural minerals consisting of hydrated silica with varying amounts of water: water opal with about 36 per cent water, ordinary opal with from 3 to 13 per cent water, and hyalite with about 3 per cent water; but none of these substances represents a compound of constant composition.

The anhydride SiO_2 occurs in rhombohedral crystals as quartz, whose prismatic faces are almost always striated horizontally; and as tridymite, also crystallizing in the hexagonal system. The amorphous silicic acid is often found mixed with the crystallized anhydride as flint, agate, chalcedony, jasper, etc. Silicic acid is, however, most frequently found in the form of its salts, the silicates.

Preparation and Properties. — Silicic acid can be very readily obtained by the hydrolysis of its fluoride,

$$3\,SiF_4 + 4\,H_2O = 2\,H_2SiF_6 + H_4SiO_4,$$

or by the decomposition of alkali silicates (water-glass) with acids:

$$Na_2SiO_3 + 2\,HCl = 2\,NaCl + H_2SiO_3.$$

The silicic acid thus obtained forms an amorphous, gelatinous mass, appreciably soluble in water and acids, and readily soluble in even dilute solutions of caustic alkalies or alkaline carbonates. Thus freshly-precipitated silicic acid will be readily and completely dissolved by a short digestion with 5 per cent (or even 1 per cent) sodium carbonate solution on the water-bath. On being dried, silicic acid gradually loses water, and at a gentle red heat is changed into the anhydride. According to the extent to which the dehydration has gone, the solubility of the silicic acid diminishes both in acids and in alkalies.

1. Air-dried silicic acid, with 16.65 per cent of water, corresponding to the formula $3\,SiO_2 \cdot 2\,H_2O$, is perceptibly soluble in acids, and completely dissolved by digestion for one-quarter to one-half an hour with 1 per cent soda solution on the water-bath.

2. *Silicic acid dried at* 100° with 13.60 per cent of water, corresponding to the formula $2\,SiO_2 \cdot H_2O$, *is practically insoluble in acids*, but can be dissolved by digesting for one-quarter hour with 1 per cent sodium carbonate solution upon the water-bath, or more readily by boiling.

3. Silicic acid dried at 200°, with 5.66 per cent of water, corresponding to the formula $5\,SiO_2 \cdot H_2O$, and the acid dried at 300°, with 3.40 per cent of water, corresponding to the formula $9\,SiO_2 \cdot H_2O$, dissolve slowly by digestion with 1 per cent sodium carbonate solution on the water-bath.

4. The anhydride obtained by gentle ignition to a faint-red heat is only partly dissolved by 1 per cent or by 5 per cent sodium carbonate after half an hour's digestion on the water-bath; but is dissolved after boiling for two hours with the sodium carbonate solution.

5. The strongly-ignited anhydride is dissolved slowly by 5 per cent sodium carbonate solution after repeated boiling for a long time, but is readily dissolved by boiling with concentrated caustic soda or potash.

6. The native anhydride, quartz, after being powdered in an agate mortar, is practically insoluble in 5 per cent sodium carbonate solution, and very difficultly soluble in boiling caustic alkali. If it is in the form of an extremely fine powder, it can be dissolved by boiling with 5 per cent sodium carbonate solution (Lunge and Millberg).

It follows from the above that the solubility of silicic acid (and of its anhydride) in alkali carbonates depends largely upon the fineness of the material.

Silicic acid, as well as its anhydride, is soluble in aqueous hydrofluoric acid, forming hydrofluosilicic acid:

$$SiO_2 + 6\,HF = 2\,H_2O + H_2SiF_6.$$

By evaporating this solution hydrofluoric acid is evolved, and silicon fluoride, with small amounts of silicic acid, is left behind. In order, then, to volatilize silicic acid completely by means of hydrofluoric acid, the hydrolytic action of water must be prevented, which is effected by the addition of a little concentrated sulfuric acid. The procedure is as follows:

Moisten the substance in a platinum crucible with a very little water, add not more than ½ cc. of concentrated sulfuric acid, and then the hydrofluoric acid. Evaporate the mixture on the water-bath, or suspend the crucible in a larger crucible, and heat the latter until the hydrofluoric acid is expelled, cool, add another portion of hydrofluoric acid and again evaporate. If a very large quantity of silicic acid is present it may be necessary to treat with hydrofluoric acid a third time. It is better to proceed in this way than to add a large quantity of hydrofluoric acid at one time. Finally drive off the sulfuric acid by heating directly over a small flame.

The salts of silicic acid, the silicates, are exceedingly numerous, and are usually very stable. Many of them are so stable that they are not attacked by concentrated mineral acids other than hydrofluoric acid, while others are easily decomposed.

The different silicates are classified according to their solubility into

A. Water-soluble silicates.

B. Water-insoluble silicates, which are again divided into

(*a*) Silicates decomposable by acids;

(*b*) Silicates undecomposable by acids.

Silicic acid is not soluble in water except to form colloidal solutions, and yields scarcely any hydrogen ions. In this respect it is a very weak acid but, as it is practically non-volatile, it is capable of expelling the acid from the salts of strong acids provided the base itself is not volatile at the temperature at which the salt is decomposed. The silicates, therefore, are very stable compounds particularly toward heat. The natural silicates are derived from orthosilicic acid, H_4SiO_4, from metasilicic acid, H_2SiO_3, and also from polysilicic acids such as $H_4Si_3O_8$, and $H_{12}Si_3O_{12}$. The solubility of the silicate depends upon two factors — the solubility of the oxide of the base and the proportion of silicic acid present. As a general rule, the salts of ortho and metasilicic acids are more soluble than those of the polysilicic acids. Thus sodium and potassium ortho and metasilicates are soluble in water, whereas a polysilicate may contain alkali as its principal base and yet be undecomposable by concentrated hydrochloric acid. Such silicates may, however, be decomposed by hydrofluoric acid, which causes volatilization of the silica as silicon tetrafluoride, by melting with a solid acid such as boric acid, or by treating with mineral acid in a sealed tube.

Salts of bases of which the ignited oxides are very insoluble, such as Al_2O_3, sometimes form insoluble silicates of the ortho and meta types.

A. Water-soluble Silicates

The silicates which are soluble in water, or "water-glasses," are obtained by fusing silica or a silicate with caustic alkali or alkali carbonate:

$$SiO_2 + Na_2CO_3 = Na_2SiO_3 + CO_2\uparrow.$$

1. **Behavior Toward Acids.** — The aqueous solution of an alkali silicate reacts strongly alkaline, showing that the salt is hydrolyzed to a marked degree:

$$SiO_3^{--} + 2\,H_2O \rightarrow 2\,OH^- + H_2SiO_3.$$

The silicic acid set free by the hydrolysis is present as hydrosole in the solution. By the addition of acid the alkali hydroxide is converted into salt and a part of the silicic acid is coagulated, provided the solution is not too dilute.

The precipitation is by no means quantitative; a considerable quantity of silicic acid remains in solution and, in fact, under some conditions all of it may remain dissolved in the dilute acid. If, namely, a 10 per cent water-glass solution is poured quickly into hydrochloric acid of specific gravity 1.1 to 1.3, there is no precipitation. After standing some time, however, the entire contents of the beaker are changed to a jelly. From 1 per cent solutions treated similarly with acid, no precipitate appears even after standing a year.

The silicic acid which is precipitated upon the addition of acid is, therefore, appreciably soluble in dilute acids. In order to separate silicic acid completely from a solution of water-glass, the hydrated acid must be changed into the less hydrated acid, $2\,SiO_2 \cdot H_2O$, by heating at 100° C. (cf. p. 440). For this purpose acidify the water-glass solution with hydrochloric acid (or nitric or sulfuric acid) and evaporate on the water-bath to complete dryness (the mass must no longer

smell of acid). Moisten the dry residue with strong acid, warm slightly, dilute and filter off the silicic acid. The small amount of silica remaining in solution can be removed almost entirely by a second evaporation of the filtrate.

2. **Behavior Toward Ammonium Salts.** — If a solution of water-glass is treated with an ammonium salt, the silicic acid will, for the most part, be precipitated as hydroxide; the precipitation is not quite quantitative, but more complete than is obtained by the addition of cold, dilute acid:

$$SiO_3^{--} + 2\,NH_4^+ \rightarrow 2\,NH_3 + H_2SiO_3;$$
$$NH_3 + H_2O \rightleftarrows NH_4OH.$$

The hydroxyl ions have a marked solvent action upon the silicic acid. For this reason the precipitation is more complete with an ammonium salt of a strong acid than with that of a weak acid, which is already hydrolyzed to a considerable extent. Boiling off the ammonia helps to make the reaction complete. The use of ammonium carbonate, though less satisfactory than ammonium chloride, is necessary when it is desired to test the solution for chloride.

Silicic acid is more completely precipitated by zinc-ammonia hydroxide than by ammonium carbonate,

$$SiO_3^{--} + [Zn(NH_3)_6](OH)_2 = 2\,OH^- + 6\,NH_3\uparrow + ZnSiO_3,$$

because the zinc silicate formed by the reaction is much more difficultly soluble in dilute alkaline solution than is the free silicic acid.

The separation of silicic acid from a solution of water-glass by means of ammonium carbonate may be illustrated by a common case. Many rocks (particularly the zircon-syenite of Norway and Greenland, many granites and basalts) contain small amounts of sodalite, $NaCl \cdot 3\,NaAlSiO_4$, a chloride silicate of the leucite group. In order to detect the chlorine in such a rock, the following process may be used: Fuse the finely powdered silicate with six times as much sodium carbonate in a platinum crucible, extract the product of the fusion with cold water and filter. The filtrate contains all of the chlorine as sodium chloride, in the presence of sodium silicate. Treat the solution with ammonium carbonate, warm gently, allow to stand twelve hours, and then filter off the precipitated silicic acid. In order to separate the rest of the silicic acid, add a little zinc-ammonia hydroxide and boil the solution until it no longer smells of ammonia. Filter off the precipitated zinc silicate and zinc oxide, acidify the filtrate with nitric acid and test for chlorine with silver nitrate.

To prepare the zinc ammonia hydroxide dissolve pure zinc in nitric acid, treat the solution with potassium hydroxide solution until it is neutral, and dissolve the filtered and washed zinc hydroxide in 6-normal ammonium hydroxide.

B. Silicates Insoluble in Water

(α) *Decomposable by Acids*

A large number of native silicates are decomposed by evaporation with hydrochloric acid, the silica being deposited sometimes in the form of a jelly and sometimes in the form of a powdery mass. All zeolites, and a number of artificial silicates (such as Portland and Roman cements) belong to this class of silicates.

To remove all of the silicic acid from these silicates, treat the finely powdered mineral with dilute hydrochloric acid and evaporate to dryness on the water-bath. During the evaporation to dryness salts like aluminum chloride (ferric chloride, etc.) are subject to hydrolysis and are converted to some extent into oxide or basic salt, insoluble in water. Therefore, in order to separate the silicic acid from the salts, it is first necessary to convert such oxides or basic salts back into chlorides. This is accomplished by moistening the dry residue with concentrated hydrochloric acid. After warming the acid with the residue for about ten minutes, dilute with hot water, boil and filter off the silicic acid using an ashless filter.

The purity of the residual silicic acid must always be tested. For this purpose, place the well-washed precipitate, together with the filter-paper, in a weighed platinum crucible which rests in an inclined position on a triangle. Dry carefully by a low flame placed in front of the crucible, and then ignite at as low a temperature as possible, with the flame now at the base of the crucible, until the carbon of the filter is all consumed. Then, for the first time, ignite strongly, cool somewhat, place in a desiccator and weigh when perfectly cool. Treat with hydrofluoric and sulfuric acids as described on p. 441, ignite and weigh after proper cooling. A difference in the weights before and after the treatment with these acids shows not only the presence of silica, but also the quantity of it. This quantitative method is necessary for the detection of small quantities of silicic acid. If the silicic acid were pure, nothing should remain after the evaporation of the sulfuric acid. Almost always a small residue of aluminium and ferric oxides remains, which in most cases can be neglected. If considerable residue is left, it should always be tested for titanic acid, barium sulfate and possibly tin dioxide.

To identify the silicic acid qualitatively, Daniel's tetrafluoride test is satisfactory.*

Daniel's Tetrafluoride Test

Ignite the well-washed precipitate, as described above, in a platinum crucible, then triturate in a mortar with three times as much potassium-sodium carbonate, and fuse the mixture in the crucible. After cooling the melt, soften it by heating with a little water and treat with dilute sulfuric acid to decompose the excess of carbonate as well as the salt of silicic acid formed during the fusion. Heat the mixture in the crucible, by placing the latter upon a piece of asbestos board, and evaporate nearly to dryness, or until a thick jelly of silicic acid remains. After cooling, add three times as much fluorspar as there was original precipitate, a little magnesite and enough concentrated sulfuric acid to make a thin paste. After mixing the contents of the crucible with the aid of a stout platinum wire, place a drop of water on the inside of a crucible cover, which is partly painted with asphaltum,

* *Z. anorg. Chem.*, **38**, 299 (1904).

place the cover on the crucible and heat the contents of the latter gently. From time to time, raise the cover to see whether the water has become turbid. It frequently happens that the water becomes turbid, and then, provided a large excess of hydrofluoric acid is present, the turbidity disappears. For this reason the cover must be inspected frequently in order not to miss any temporary turbidity.

(β) *Silicates Undecomposable by Acids*

Most silicates, the feldspars, micas, artificial glasses, porcelain, etc., belong to this class. In order to remove the silicic acid from such substances, they must be

1. Fused with an alkali carbonate.
2. Fused with lead oxide or boron trioxide, or
3. Heated with sulfuric and hydrofluoric acids.

The effect of fusing a silicate with an alkali carbonate, or with a fusible oxide of some metal such as lead, is to increase the proportion of base in the silicate molecule. When the proportion of base is increased, the solubility of the silicate is also increased provided the base is itself readily soluble in acid. It is not at all necessary, therefore, to get all the silicic acid in the form of sodium silicate or of lead silicate, by fusing with sodium carbonate or with lead oxide, but it is sufficient if the silicate is converted into a silicate which is decomposable by acid. For this reason the fusion with sodium carbonate or with lead oxide is often said to *open up* the silicate. It converts the silicate into the ortho or meta type and makes the silicate decomposable by acid. Thus after fusing with sodium carbonate, for example, it will be found that part of the sodium is converted into water-soluble sodium silicate and part of it into a double silicate which is decomposable by acid. A part of the sodium and a part of the silicate can be dissolved out of the fused mass by treatment with hot water.

The tetrafluoride test for silicic acid is very sensitive if the reaction is carried out in a very small platinum crucible. If such a crucible is not at hand, with a capacity of say 0.5 to 1 cc., it is better to test by the quantitative method if less than 0.01 gm. of silicic acid is present.

1. *Fusion with an Alkali Carbonate.* — This method is commonly used when it is desired to detect the presence of silicic acid and of all the bases except the alkalies.

Mix the finely powdered substance with 4–6 times as much calcined sodium carbonate (or a mixture of equal parts of sodium and potassium carbonates, which melts lower than sodium carbonate alone), and fuse the mixture in a platinum crucible, heating carefully at first to avoid spattering from too violent evolution of carbon dioxide. Gradually increase the temperature until the full heat of the burner is reached, and continue fusing until the molten mass is quiet, and then heat for about a quarter of an hour over the blast lamp. Make a spiral by winding some platinum wire around a stirring rod, and insert the spiral in the melt. Cool the crucible quickly by directing a blast of cold air against its sides, and while the contents of the crucible are still warm, but not hot enough to spatter badly on the water, cover with a little water from the wash bottle. After a few minutes the fusion can usually be withdrawn with the aid of the platinum spiral. Treat the product of the fusion as described under (α).

2. *Fusion with Lead Oxide or Boron Trioxide.* — These methods are very rarely used in qualitative analysis, so that it will not be necessary to describe them here. They play a more important part in quantitative analysis and will be described, therefore, in the second volume of this book.

3. *Decomposition by Hydrofluoric Acid.* — This method is used principally when a silicate is to be examined for alkalies, titanic acid or barium.

Treat the finely powdered silicate in a platinum dish with about 2 cc. of pure sulfuric acid (1 vol. concentrated acid and 2 vols. of water) and about 5 cc. of pure 48 per cent hydrofluoric acid. Evaporate the mixture on the water-bath, stirring the mass from time to time with a thick platinum wire until it no longer smells of hydrofluoric acid. Add 5 cc. more of hydrofluoric acid and again evaporate, finally heating the dish very carefully over the free flame, under a good hood, until the greater part of the sulfuric acid is expelled. The mass should not be ignited strongly, for a part of the sulfate may then be changed to an oxide insoluble in water. The sulfates of iron and aluminium, for example, are decomposed on ignition. After cooling, treat the mass with water, and usually everything will gradually go into solution. If a residue remains, test it for barium sulfate, titanic acid and tinstone. The solution can be used for the alkali tests, or for the tests for the other metals, if it is desired.

Reactions in the Dry Way

If silicic acid or a silicate is heated in the salt of phosphorus bead, the metallic oxide will dissolve, while the silicic acid itself will be left as a white gelatinous mass, suspended in the bead (skeleton bead). This reaction, however, is not infallible, for certain silicates of the zeolite group dissolve in the bead without the formation of the skeleton.

SILICON, Si. At. Wt. 28.3

Silicon exists in two modifications, one of which is crystalline, while the other is amorphous. Amorphous silicon is a dark-brown powder, which can be oxidized by heating in the air. The crystalline modification remains unchanged on ignition in pure air or in oxygen, but if the air contains carbon dioxide, it is oxidized to silicon dioxide with deposition of carbon:

$$CO_2 + Si = SiO_2 + C.$$

Crystallized silicon is not attacked by any acid, but is readily dissolved by boiling with concentrated caustic alkali with evolution of hydrogen:

$$Si + 2\,OH^- + H_2O \rightarrow SiO_3^{--} + 2\,H_2\uparrow.$$

Silicon unites with many metals, forming silicides. The silicides of the light metals, magnesium, calcium, etc., are decomposed by dilute hydrochloric acid with the formation of spontaneously-combustible silicon hydride:

$$Mg_2Si + 4\,H^+ \rightarrow 2\,Mg^{++} + H_4Si\uparrow.$$

The hydride of silicon is not spontaneously combustible when pure, only when it is contaminated with hydrogen, as is invariably the case.

In order to detect the presence of silicon in such a compound, treat it with nitric acid, which oxidizes the greater part of the silicon to silicic acid.

Detection of Silicon in Iron and Steel

If it is a question of detecting the presence of silicon in the different kinds of ferrous alloys (steel, cast iron, etc.), take a large quantity of material, for the amount of iron silicide present is usually very small. Place 5 or 10 gms. of the material (best in the form of borings) in a large beaker and treat with 60 cc. of 6-normal nitric acid. A violent reaction at once takes place with evolution of brown nitrous fumes. As soon as this action lessens, heat the solution to boiling, and continue heating until no more brown fumes are given off. Pour the solution into a 200-cc. casserole and evaporate as far as possible upon the water-bath. Heat the residue carefully over a free flame until it is perfectly dry and then ignite the mass until the nitrate is completely changed to oxide, when no more brown fumes will be evolved. After cooling, dissolve the mass in about 50 cc. of concentrated hydrochloric acid, heat with constant stirring almost to boiling, evaporate nearly to dryness, take up in water, filter, and test the residue for silicic acid, by seeing whether it is volatile with sulfuric and hydrofluoric acids.

In the analysis of cast iron, the silicic acid obtained is contaminated with graphite, which can be removed by long ignition in a platinum crucible before treating with hydrofluoric and sulfuric acids.

Detection of Silicon in Carborundum and Metal Silicides

Other silicides, such as carborundum, SiC, are not decomposed by nitric acid; they can be fused with caustic alkali in a silver crucible,

$$SiC + 4\,KOH + 2\,H_2O = K_2SiO_3 + K_2CO_3 + 4\,H_2\uparrow,$$

and on acidifying the melt, the silicic acid separates out. During the fusion the liberated hydrogen takes fire and forms water with the oxygen of the air.

Carborundum in the form of a fine powder is also easily decomposed by fusing with potassium carbonate. On removing the cover of the platinum crucible the blue flame of burning carbon monoxide is seen:

$$3\,K_2CO_3 + SiC = K_2SiO_3 + 2\,K_2O + 4\,CO\uparrow.$$

The method of fusing silicides with caustic alkali is often used for getting metallic silicides into solution. Many copper silicon alloys are scarcely attacked by even aqua regia. If, however, they are fused with caustic alkali in a silver crucible, potassium silicate, metallic copper, and hydrogen are formed:

$$SiCu_2 + 2\,OH^- + H_2O = SiO_3^{--} + 2\,Cu + 2\,H_2\uparrow.$$

By treating the melt with water, the soluble potassium silicate may be separated from the copper.

PART IV. SYSTEMATIC ANALYSIS

The purpose of qualitative analysis is not simply to find out what elements are contained in a given substance, but the aim should also be to get a good idea of the relative amounts that are present. Manganese chloride, for example, is made from pyrolusite, and almost always contains traces of calcium, magnesium, nickel, cobalt, and iron. If the analyst should report that "the analyzed substance consists of chlorides of calcium, magnesium, nickel, cobalt, iron, and manganese," it is evident that one would get but a poor idea of the nature of the substance. The report should read: "The substance examined was manganese chloride, and contained traces of calcium, magnesium, etc., as impurities."

In order to be able to estimate the relative amounts of the different components of a substance, it is necessary to start with a known amount (usually $\frac{1}{2}$ to 1 gm.) and compare the size of the precipitates produced. It will be impossible for the beginner to estimate the amount of a precipitate obtained, if he has studied the reactions of the elements with unknown amounts of the different substances. If, however, he has learned to work with a known amount of material, he will soon be able to judge from the size of a precipitate the amount of element to which it corresponds.

It is a good plan first to work through the analysis of each group with a known solution containing 20 mgms. of each element and then it is comparatively easy to determine approximately how much of each element is present by the test obtained in the analysis of any unknown. Thus, starting with 1 gm. of the original substance, it is often convenient to designate a constituent as present in *small* quantity when apparently less than 10 mgms. is found, as present in *medium* quantity when from 10 to 50 mgms. is found, and as present in *large* quantity when distinctly more than 50 mgms. is present. Experience with large classes of students has shown that such judgments are correct in nearly nine cases out of ten. It should be borne in mind, moreover, that for estimating small quantities of substances, qualitative tests are *more accurate* than any method of quantitative analysis. Thus all colorimetric methods of quantitative analysis are really based on qualitative tests. The comparison of a test with one obtained using a *known quantity* of substance often gives a more exact determination of the

quantity present than a method involving weighing or titration. This is because it is easy to prepare a solution containing say 1 mgm. per cubic centimeter with an error of less than 5 parts per thousand, by dissolving 1000 times as much in a liter and thoroughly shaking; but it is more difficult to determine by direct weighing and with equal accuracy the presence of only 1 mgm. of substance. By the process of diluting and taking an aliquot part, it is possible to prepare a solution containing a very small known quantity of any soluble substance. For convenience, it is well to have solutions at hand containing exactly 10 mgms. per cubic centimeter of each constituent. By taking three small drops of such a solution, approximately 1 mgm. of the constituent can be obtained.

Every analysis should be divided into three parts:

I. *The preliminary examination.*
II. *The examination for the metals* (*cations*).
III. *The examination for the negative elements* (*anions*).

The substance analyzed may be

A. *Solid* and *non-metallic.*
B. *A metal* or *an alloy.*
C. *A solution* (*liquid*).
D. *A gas.*

The whole amount of the substance at hand should never be used for the first analysis, but a portion should always be reserved for unforeseen accidents. The portion taken for analysis should be divided into two parts after the preliminary examination, the first part being used for the tests for the basic constituents and the other part for the tests for the acidic constituents.

Before beginning an analysis, the substance should be carefully examined with the naked eye and with the microscope, and the results noted. Oftentimes the odor, color, and crystalline form suffice to give important clues as to the nature of the substance.

A. THE SUBSTANCE IS SOLID AND NON-METALLIC*

I. Preliminary Examination

This should never be omitted, for it often shows how the subsequent analysis may be considerably shortened, and in some cases makes the further examination unnecessary. It consists only of making the following few simple tests:

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* See p. 492 for B and C.

1. **Heating in the Closed Tube.** — By a closed tube is understood a small glass tube about 10 cm. long and 0.5 cm. in diameter sealed at one end. Place a little of the substance in the tube so that none of it remains adhering to the sides, hold the tube in a nearly horizontal position and cautiously heat in the flame, noting carefully whether any change takes place.

The Substance is Volatile

(*a*) *The substance sublimes completely* without any deposition of water; it contains no non-volatile substance.

The sublimate is white. The halogen compounds of ammonium,* mercuric and mercurous chloride and bromide, mercuric aminochloride, arsenic trioxide and arsenic pentoxide may be present.

Arsenic pentoxide melts before being changed into the trioxide.

The sublimate is colored —

Gray: all oxygen compounds of mercury, cyanide of mercury, free iodine, and arsenic.

Mercuric cyanide leaves a brown mass, paracyanide, which only disappears after long-continued heating.

Yellow: arsenic sulfide, sulfur, mercuric iodide.

Mercuric iodide becomes red immediately on being rubbed with a glass rod.

Grayish black: mercuric sulfide.

(*b*) *The substance is completely volatile, with separation of water* and gaseous products: most ammonium compounds (with the exception of those of the halogens) and free oxalic acid.

By very cautious heating, oxalic acid may be sublimed; it usually decomposes, however, into water, carbon monoxide, and carbon dioxide.

The Substance is only Partly Volatile

In this case gases and vapors may be evolved:

Oxygen from peroxides, nitrates, chlorates, iodates, etc.

Carbon dioxide from carbonates and organic substances; in the latter case it is usually accompanied with the separation of carbon and evolution of empyreumatic, combustible vapors.

Chlorine from chlorides of platinum, gold, copper, iron, etc.

Iodine from iodides, in the presence of oxidizing substances.

Sulfur from many sulfides and thiosulfates.

* In the case of ammonium salts, e.g., NH_4Cl, this is not a true sublimation. When heated NH_4Cl gives NH_3 and HCl gases which combine again when chilled.

Arsenic from arsenites and arsenates, in the presence of carbon or organic substances.

Arsenites are reduced without the aid of charcoal:

$$10\,K_3AsO_3 = 6\,K_3AsO_4 + 6\,K_2O + As_4.$$

Water from substances containing water of crystallization, from acid salts, organic substances, or from the phosphate, borate, chromate, vanadate, and tungstate of ammonium.

The water given off condenses in the cooler part of the tube and should be tested with litmus-paper. If it reacts alkaline, it comes from ammonium compounds; if acid, it results from easily decomposable salts of the stronger acids.

Many fluorides when heated with water give off hydrofluoric acid, which etches the glass.

If a sublimate is formed, make the following experiment:

Mix a little of the substance with three times as much calcined sodium carbonate and heat in the closed tube. If *ammonium salts* are present, the smell of ammonia can be detected. *Mercury* compounds give a deposit of gray metal (cf. p. 215); *arsenic* and its oxygen compounds also usually yield the gray metal (but no globules), accompanied by a garlic odor.

The oxygen compounds of arsenic do not give the metal when heated with pure sodium carbonate. Commercial sodium carbonate, however, is usually contaminated with enough paper fibres to cause the reduction.

2. **Test the Substance in the Bead.** — Make a borax or sodium phosphate bead in the loop of a very thin platinum wire (as described on p. 65), introduce it with a little of the substance into the oxidizing flame, observe the color of the bead both when it is hot and when it is cold, and then heat it in the reducing flame. Borax is usually used for this experiment, except when it is desired to test for silicic or titanic acids, or when the substance is white, in which case salt of phosphorus is used. Only colored oxides are capable of coloring the borax bead.

Some oxides are reduced to metal, so that the bead appears gray in the reducing flame (see following table). $CuSO_4$ is white when anhydrous, but becomes blue immediately on the addition of water.

The following substances impart a characteristic color to the bead: iron, manganese, nickel, cobalt, chromium, uranium, copper (didymium, cerium, vanadium, titanium, and tungsten).

Since the coloration varies with the temperature and with the amount of substance used, the results to be expected, with the necessary conditions, are summarized in the table on p. 453. The following

abbreviations are used: h = hot; c = cold; h-c = hot and cold; s.s. = slightly saturated; sat. = saturated.

Color of the Bead.	With Borax.		With Salt of Phosphorus.	
	In the Oxidizing Flame.	In the Reducing Flame.	In the Oxidizing Flame.	In the Reducing Flame.
Colorless	SiO_2 (without skeleton), alkaline earths, Hg, Pb, Bi, Sb, Cd, Zn, Sn, Ti	SiO_2 (without skeleton), alkaline earths and earths, Mn, Di, Ce, Cu (s.s.)	SiO_2 (usually with skeleton), alkaline earths and earths (sat. = turbid)	SiO_2 (usually with skeleton), alkaline earths and earths, Mn, Di, Ce, Cu (s.s.)
	W, Mo, Fe (s.s.—c)		W, Ti	
Gray		Ag, Pb, Bi, Sb, Cd, Zn, Ni		Ag, Pd, Bi, Sb, Cd, Zn, Ni
Yellow (or brown)	Fe (s.s.—h), Ag (h), Ce (h), U (h), V (h—sat.), Ni (c) (brown)	Ti (h), W (h) V (h), Mo (h)	Fe (s.s.—h), Ag (h), Fe (sat.—c), Ce (h), V (h), U (h), Ni (c) (brown)	Fe (h), Ti (h)
Green	Cr (c), Cu (h)	Fe (h—c), Ur, Cr. V (h)	Cr (c), Cu (h), Mo (h), U (c—sat.)	Cr (c), U (c), V (c), Mo (c)
Blue	Co (h—c), Cu (c)	Co (h—c)	Co (h—c), Cu (c)	Co (h—c), W (c)
Violet	Mn (h—c), Di (h—c), and Ni (with cobalt)		Mn (h—c), Di (h—c)	Ti (c)
Red	Fe (h—sat.) Ce (h)	Cu (sat.), opaque; when very slightly saturated and with a trace of Sn, ruby red and transparent.	Fe (h—sat.) Ce (h)	Cu as in the borax bead; Ti and W in the presence of iron = blood red

3. **Heat a Little of the Substance upon Charcoal before the Blowpipe;** if deflagration takes place a nitrate, nitrite, chlorate, iodate, etc., may be present.

4. **Heat the Substance with Soda upon Charcoal before the Blowpipe.** — Mix as much of the substance as can be taken up on the end of a knife-blade with twice as much sodium carbonate (as described on p. 69), place it in a cavity on a piece of charcoal and heat in the reducing flame of the blowpipe.

There is obtained:

(*a*) Metal without incrustation.	As malleable button: **Au, Ag, Sn, Cu,** which can be pressed flat in an agate mortar. As gray metallic particles: **Pt, Fe, Ni,** and **Co.** **Pt** may be pressed flat in an agate mortar; **Fe, Ni,** and **Co** are magnetic and are attracted by a magnet (cf. p. 67).
(*b*) Metal with incrustation ...	As a brittle metallic button: **Sb** (white incrustation), **Bi** (yellow incrustation). The button may be reduced to a powder by grinding in an agate mortar. As a malleable button: **Pb** (yellow incrustation).
(*c*) Incrustation without metal.	White, yellow when hot: **Zn.** Brown: **Cd.** White: **As** (garlic odor).
(*d*) White, infusible, strongly luminous mass	**Ca, Sr, Mg, Al,** and rare earths.

(*e*) **Sulfur** compounds are reduced to sulfides. If the melt is placed on a bright silver coin and moistened with water, the silver is blackened (Hepar reaction).

5. **Test the Substance to See whether it Imparts Any Color to the Non-luminous Flame.** — Introduce a little of the substance on a platinum wire into the base of the flame (cf. p. 63), and then into the fusing zone. Afterwards moisten it with dilute hydrochloric acid and repeat the experiment. The following indications may be obtained:

Sodium gives a yellow monochromatic flame; a piece of sealing-wax or a crystal of potassium dichromate appears yellow when illuminated by this flame.

Potassium (cesium and rubidium) gives a violet flame which is completely obliterated by the sodium flame. If the flame is observed through cobalt glass, the sodium flame disappears and the potassium flame appears pink.

Lithium gives a carmine-red flame (or a red line in the spectroscope).

Strontium also gives a carmine-red flame (which the spectroscope shows to consist of several lines in the orange, and a bright line in the blue).

Calcium gives a brick-red flame (in the spectroscope an orange and a green line are seen, both about an equal distance away from the sodium line).

Barium gives a greenish-yellow flame.

In the case of barium sulfate the green flame is either indistinct

or not visible. In order to detect barium in this case, heat a small portion of the substance in the upper reducing flame, cool, moisten with hydrochloric acid (odor of hydrogen sulfide) and again heat, when the barium flame can be easily seen.

Thallium gives an emerald-green flame.

If a green flame is obtained, test another portion of the substance for boric acid, by treating with concentrated sulfuric acid and bringing near the flame. A green color indicates the presence of boric acid, but if copper is present this test is not reliable.

By heating the solid substance with potassium ethyl sulfate in a test-tube, boric acid is converted into $B(OC_2H_5)_3$, which is volatile and burns with a green flame. Copper chloride does not interfere with this test.

Lead, Arsenic, Antimony color the flame light blue, and **copper** compounds color the flame either green or blue.

Preliminary Examination for the Acidic Constituents (Anions)

1. **Dilute Sulfuric Acid** (2-normal). — Treat about a gram of the substance in a small test-tube with dilute sulfuric acid, and note whether a reaction takes place in the cold or not (evolution of a gas).

The following gases can be recognized:

HCN from cyanides (odor);

Mercuric cyanide does not liberate HCN in this test.

H_2S from soluble sulfides (odor, and blackening of lead acetate paper);

NO_2 from nitrites (brown fumes);

SO_2 without separation of sulfur from sulfites (odor of burning sulfur);

SO_2 accompanied by separation of sulfur from thiosulfates; the deposited sulfur is yellow, particularly after warming;

CO_2 from carbonates or cyanates (barium hydroxide solution is rendered turbid).

By boiling with dilute sulfuric acid, soluble *ferro-* and *ferri-cyanides* are decomposed and evolve hydrocyanic acid; *acetates* set free acetic acid; *hypochlorites* evolve chlorine (which also takes place in the cold); while the *peroxides of the alkalies* and alkaline earths are decomposed with evolution of oxygen.

Alkali peroxides also evolve oxygen when treated with water. Cf. p. 88.

2. **Concentrated Sulfuric Acid.** — If the substance does not react with dilute sulfuric acid, add 3 or 4 cc. of concentrated sulfuric acid

and heat. If the substance reacted with dilute sulfuric acid, it will react violently with concentrated sulfuric acid and the gas will come off so quickly that it will carry small particles of the sulfuric acid with it, which makes the gas appear to have a penetrating odor and may lead to a mistaken conclusion, especially as it will also cause barium hydroxide solution to become turbid.

In such a case, add dilute sulfuric acid drop by drop to a new portion of the substance until no further action takes place, then add 5 cc. of concentrated sulfuric acid and heat the mixture.

Gases and vapors may be evolved, which are

(*a*) *Colorless*

HCl from chlorides, fuming in the air, with penetrating odor. The fumes do not cause a turbidity with water.

AgCl and $HgCl_2$ evolve HCl very slowly; the same is true of Hg_2Cl_2, and in this case SO_2 is also set free. Cf. p. 309.

SiF_4 from fluorides, fuming in the air, with a penetrating odor, and causing a turbidity on coming in contact with water.

SiF_4 is formed on account of the experiment being performed in glass. In platinum and in the absence of silica, H_2F_2 would be evolved, which does not render water turbid.

SO_2, without separation of *sulfur*. If there was no evolution of sulfur dioxide on treatment of the substance with dilute sulfuric acid, the sulfur dioxide which now escapes must come from the sulfuric acid itself; a metal, sulfur, a sulfide, carbon, or non-volatile organic matter, such as tartaric acid, citric acid, sugar, starch, etc., must be present. If non-volatile organic matter is present, carbonization will take place on warming.

SO_2 with separation of *sulfur* indicates the presence of a sulfocyanate, in case there was no action with dilute sulfuric acid.

CO from oxalates and other organic substances, and cyanates. It is an odorless gas, which does not fume in the air and burns with a blue flame.

(*b*) *Colored*

Cl_2, a yellow gas with a suffocating odor, turns iodo-starch paper blue, and indicates the presence of both a chloride and an oxidizing substance.

ClO_2, a yellow gas, very similar to chlorine, but which explodes violently on being heated, indicates a chlorate. If the substance deflagrates on being heated on charcoal, only a small portion of the

substance should be used for the test with concentrated sulfuric acid; but if no explosion takes place on warming, more of the substance should be added.

HBr from bromides has a penetrating odor, fumes in the air, and is always colored yellowish brown by the presence of small amounts of bromine. The sulfuric acid is at first colored brown in the case of a colorless bromide, but becomes colorless on being boiled.

CrO_2Cl_2, brown (similar to bromine), results from the presence of a chloride and chromic acid.

I_2, violet. In the case of a colorless iodide, the sulfuric acid is at first colored brown by small amounts of iodide, and gray, solid iodine is deposited if considerable iodide is present, which volatilizes on warming, forming violet vapors. If considerable iodide is used for this test, the sulfuric acid is reduced to SO_2, or even H_2S (cf. p. 321).

Mn_2O_7, violet, is formed from permanganic acid, and is decomposed with scintillation, often exploding, on being warmed.

NO_2, brown, with a penetrating odor, comes from nitrates.

After the preceding tests have been made, the next step is

Dissolving the Substance

As solvents the following are used:

1. Water;
2. Hydrochloric acid;
3. Nitric acid;
4. Aqua regia.

In most cases the first three solvents suffice, aqua regia being seldom necessary, as will be seen from the following table:

Qualitative analysis is based largely upon the different solubilities of typical salts. The measurement of the solubility, or quantity dissolved by a given volume of solvent, has occupied the attention of a great many chemists and books have been written on this subject alone. All such data, however, when brought together and compared show that numerical values for the weight of solid dissolved by 100 grams of water are hard to determine accurately for those very substances with which the analytical chemist is concerned, namely the less soluble ones.

There are several ways of determining the solubility of a substance. One method is to shake an excess of the solid at a constant temperature until no more of the substance dissolves. Another method is to obtain a supersaturated solution of the substance and allow it to stand until no more of the salt deposits. A third method consists in forming the substance by metathesis and finding how much of the constituents must be present in order to obtain precipitation.

Unfortunately, every method of measurement involves some unavoidable error and in the case of very insoluble substances this error is sometimes much larger than the actual quantity of substance dissolved. For example, if one were to determine the solubility of silver cyanide by taking a weighed quantity and finding

SOLUBILITY TABLE *

	Sodium, Na^+.	Potassium, K^+.	Ammonium, NH_4^+.	Magnesium, Mg^{++}.	Calcium, Ca^{++}.	Strontium, Sr^{++}.	Barium, Ba^{++}.	Aluminium, Al^{+++}.	Chromium, Cr^{+++}.
Acetate, $C_2H_3O_2^-$	W	W	W	w	W	w	w	W	w
Arsenate, AsO_4^{---}	W	W	w	a	a	a	a	a	a
Arsenite, AsO_3^{---}	W	W	w	a	a	a	a	—	—
Borate, BO_3^{---}	W	W	w	w-a	a	a	a	a	a
Bromide, Br^-	47.5	39.4	41.9	58.	58.8	50.	51.	w	w&i
Carbonate, CO_3^{--}	17.6	53.2	50.0	9.7×10^{-2}	1.3×10^{-3}	1×10^{-3}	2×10^{-3}	—	—
Chlorate, ClO_3^-	49.7	6.78	w	56.3	63.6	64.	20.6	w	w
Chloride, Cl^-	26.4	25.5	27.1	35.3	42.7	35.0	26.3	w	58.5†
Chromate, CrO_4^{--}	44.6	38.6	28.8	42.0	2.33	0.12	3.5×10^{-4}	—	a
Cyanide, CN^-	W	W	w	w	w	w	w-a	—	a
Ferricyanide $[Fe(CN)_6]^{---}$	W	W	w	w	w	w	w	—	—
Ferrocyanide $[Fe(CN)_6]^{==}$	W	W	w	w	w	w	w-a	—	—
Fluoride, F^-	4.22	48.0	W	8.7×10^{-3}	1.6×10^{-3}	1.2×10^{-2}	0.16	a	w-a
Hydroxide, OH^-	51.7	53.4	W	9×10^{-4}	3.6	0.69	3.4	A	A
Iodide, I^-	64.2	59.1	62.5	59.7	67.1	64.2	66.5	w	w
Nitrate, NO_3^-	46.8	24.1	68.2	43.1	54.8	41.5	7.9	W	W
Oxalate, $C_2O_4^{--}$	3.7	W	2.2	3×10^{-2}	6×10^{-4}	4.6×10^{-3}	1×10^{-2}	a	w-a
Oxide, O^{--}	w	w	—	A	W-A	W	W	A-I	A-I
Phosphate, PO_4^{---}	9.5	W	W	5.5×10^{-3}	2×10^{-2}	A	4.9×10^{-5}	A	a
Silicate, $SiO_4^{==}$	W	W	—	a	a	a	a	A-I	a
Sulfate, SO_4^{--}	16.0	10.0	43.0	26.2	0.21	1.1×10^{-2}	2.4×10^{-4}	26.6	W-I
Sulfide, S^{--}	15.3	W	W	a	0.2	W	w	a	a-i
Thiocyanate, CNS^-	W	68.5	61.8	w	w	w	w	w	w
Tartrate, $C_4H_4O_6^{--}$	W	W	W	w-a	a	a	a	w	w

W or w, soluble in water; A or a, insoluble in water, soluble in HCl, HNO_3 or aqua regia; I or i, insoluble in water and in HCl, HNO_3 or aqua regia; W-A or w-a slightly soluble in water but more soluble in acids; W-I or w-i, slightly soluble in water and slightly soluble in acids; A-I or a-i, insoluble in water, slightly soluble in acids. Capitals are used for the more important substances, small letters for the unimportant ones. The salts referred to are generally considered as normal. Acid and basic salts are omitted in this table. Where numbers are given, they represent the grams of substance that dissolve in 100 cc. of water at temperature of the laboratory. The values, in some cases, are only approximate.

* Based on the table in Fresenius' Qualitative Analysis. † Sublimed $CrCl_3$ is insoluble in water.

SOLUBILITY TABLE

	Zinc, Zn^{++}	Manganese, Mn^{++}	Nickel, Ni^{++}	Cobalt, Co^{++}	Ferrous, Fe^{++}	Ferric, Fe^{+++}	Silver, Ag^{+}	Lead, Pb^{++}	Mercurous, Hg_2^{++}
Acetate, $C_2H_3O_2^-$	W	w	w	w	w	W	w	W	w-a
Arsenate, AsO_4^{---}	a	a	a	a	a	a	a	a	a
Arsenite, AsO_3^{---}	—	a	a	a	a	a	a	a	a
Borate, BO_3^{---}	a	a	a	a	a	a	a	a	—
Bromide, Br^-	82.5	58.8	56.5	w	54.3	w	8.4×10^{-6}	0.84	3.9×10^{-6}
Carbonate, CO_3^{--}	A	A	A	A	A	—	a	6×10^{-5}	a
Chlorate, ClO_3^-	66.3	w	57.3	64.2	w	w	w	60.2	w
Chloride, Cl^-	78.6	43.6	39.0	33.3	41.2	47.9	1.5×10^{-4}	0.96	2.1×10^{-4}
Chromate, CrO_4^{--}	w	w	a	a	—	w	2.5×10^{-3}	2×10^{-5}	a
Cyanide, CN^-	A	a	a-i	a-i	a-i	—	2.2×10^{-5}	a	—
Ferricyanide $[Fe(CN)_6]^{---}$	a	I	I	I	I	w	I	w-a	—
Ferrocyanide $[Fe(CN)_6]^{====}$	A-I	a	I	I	I	I	I	a	—
Fluoride, F^-	a	w-a	w-a	w-a	w-a	w	57.5	6.4×10^{-2}	w
Hydroxide, OH^-	1.3×10^{-4}	1.9×10^{-4}	A	A	7×10^{-4}	A	2×10^{-3}	1.9×10^{-3}	—
Iodide, I^-	81.2	W	59.7	61.2	W	W	3.5×10^{-7}	0.06	A
Nitrate, NO_3^-	53.9	62.4	49.1	49.7	45.5	W	68.3	34.3	W
Oxalate, $C_2O_4^{--}$	6.4×10^{-4}	w-a	a	a	a	a	3.5×10^{-3}	1.8×10^{-4}	a
Oxide, O^{--}	A	A	A	A	A	A	A	A	A
Phosphate, PO_4^{---}	A	A	A	A	A	A	6.4×10^{-4}	1.3×10^{-5}	a
Silicate, $SiO_4^{====}$	a	a	a	a	a	a	—	a	—
Sulfate, SO_4^{--}	36.6	38.6	25.5	25.7	21.0	W	0.80	4.3×10^{-2}	W
Sulfide, S^{--}	3.3×10^{-9}	3.3×10^{-5}	7×10^{-10}	7×10^{-10}	3×10^{-7}	3×10^{-7}	1×10^{-12}	4.9×10^{-11}	A
Thiocyanate, CNS^-	w	w	w	w	w	w	1.4×10^{-4}	4.5	A
Tartrate, $C_4H_4O_6^{--}$	a	w-a	a	W	w-a	W	a	a	w-a

SOLUBILITY TABLE

	Mercuric, Hg^{++}.	Cupric, Cu^{++}.	Bismuth, Bi^{+++}.	Cadmium, Cd^{++}.	Stannous, Sn^{++}.	Stannic, Sn^{++++}	Antimonous, Sb^{+++}.	Gold, Au^{+++}.	Platinum, Pt^{++++}.
Acetate, $C_2H_3O_2^-$	w	W	w	w	w	w	—	—	—
Arsenate, AsO_4^{---}	a	a	a	a	—	—	—	—	—
Arsenite, AsO_3^{---}	a	a	a	a	—	—	—	—	—
Borate, BO_3^{---}	—	a	a	w-a	a	—	—	—	—
Bromide, Br^-	0.61	w	w-a	48.8	w	w-a	w-a	w	w
Carbonate, CO_3^{--}	a	A	a	a	—	—	—	—	—
Chlorate, ClO_3^-	w	62.4	w	76.5	w	—	—	—	—
Chloride, Cl^-	6.89	43.1	W-A	56.3	73	W	W-A	W	W
Chromate, CrO_4^{--}	w-a	w	a	a	a	—	—	—	—
Cyanide, CN^-	W	a	—	a	—	—	—	W	w
Ferricyanide $[Fe(CN)_6]^{---}$	i	—	i	a-i	i	—	—	w	w
Ferrocyanide $[Fe(CN)_6]^{==}$	—	I	i	a-i	i	i	—	—	—
Fluoride, F^-	w-a	a	w	w-a	w	w	w	—	—
Hydroxide, OH^-	5×10^{-3}	A	A	2.6×10^{-4}	—	A	A	—	—
Iodide, I^-	6×10^{-3}	4.3×10^{-4}	a	46.0	0.97	w	w-a	a	i
Nitrate, NO_3^-	W	55.6	W-A	58.4	—	—	—	—	w
Oxalate, $C_2O_4^{--}$	a	a	a	3.7×10^{-3}	a	w	a	—	—
Oxide, O^{--}	A	A	A	A	A	A-I	A	—	a
Phosphate, PO_4^{---}	a	A	a	a	a	A	w-a	—	—
Silicate, $SiO_4^{==}$	—	a	—	a	—	—	—	—	—
Sulfate, SO_4^{--}	6×10^{-2}	17.4	w-a	43.4	W	—	—	—	w
Sulfide, S^{--}	4.6×10^{-28}	8.8×10^{-20}	A	8.6×10^{-12}	A	A	A	A	A
Thiocyanate, CNS^-	W	a	—	w-a	—	w	—	—	a
Tartrate, $C_4H_4O_6^{--}$	a	w	a	w-a	a	—	a	—	—

how much was left after shaking with water, or by finding how much salt was left after evaporating the water to dryness, the analytical error involved could amount easily to 0.0010 gram and only about 0.0002 gram of the salt really dissolves. When we remember that some of the solubility measurements were made many years ago, it is not strange that there should be disagreements of this nature.

The difficulties involved in the measurement of the solubilities of crystalline substances are bad enough but the case is much worse with amorphous or gelatinous substances. When shaken with water for some time, any finely-divided substance tends to form a suspension which will pass through ordinary filter paper and gelatinous substances form colloidal solutions. It is almost impossible to draw the line closely between true solutions, colloidal solutions, and suspensions. Errors in determining the solubility due to the formation of colloidal solutions and suspensions may be enormous.

There are other difficulties involved. In actual analytical work, the chemist rarely has time to wait for perfect equilibrium to take place. In dissolving a substance, he usually gets an under-saturated solution and in making precipitations he usually gets a supersaturated solution. Moreover many substances like nickel sulfide, aluminium hydroxide and silicic acid, appear to be much more insoluble after they have stood in the air a short time than when freshly precipitated and although nickel sulfide is harder to precipitate than zinc sulfide, the latter dissolves more readily in cold, dilute acid.

Nearly twenty years ago, the writer attempted to collect data concerning the solubilities of the more important substances involved in the qualitative procedure and found so much disagreement in the values obtained by skillful workers that the task was abandoned. So, in the early editions of this book, this section was headed "Solubility Table" but there was no attempt made to give numerical values for the solubility of any substance. Later, Dr. Treadwell introduced a table of Solubilities and Solubility Products (cf. p. 21), but left out values for those substances which are of most importance in qualitative analysis. Some of these values, however, were supplied in the English text and were taken from the tables of Landolt-Börnstein. Allowance was not made for the fact that many of these salts hydrolyze in very dilute solution; this also causes considerable error. In the English text there was also inserted a Solubility Table based upon that given in the book of Fresenius-Wells, because experience has shown the helpfulness of such a table.

In the seventeenth edition of C. R. Fresenius' well-known text, which has been revised and edited by H. Fresenius, E. Hintz, T. W. Fresenius, H. Weber, L. Grünhut, R. Fresenius and L. Fresenius, data is given for about 180 salts and most of these values are shown in the Solubility Tables on pages 458, 459, and 460, of this book.

This table, in the Fresenius book, is given on the last page of the book and there appears to be no reference to it in the text; there is also no mention of how the values were obtained.

To illustrate how unreliable and how misleading such tables may be, take the values given for the solubilities of zinc, manganese, nickel, cobalt, ferrous, ferric, silver, lead, mercury, copper and cadmium sulfides. According to the table in this seventeenth edition of Fresenius (1919), 100 grams of saturated solution at 18° contain 6.9×10^{-4} g. ZnS, 4.8×10^{-4} g. MnS, 3.6×10^{-4} g. NiS, 3.8×10^{-4} g. CoS, 6.2×10^{-4} g. FeS, 4.9×10^{-4} g. Fe_2S_3, 1.4×10^{-7} g. Ag_2S, 8.6×10^{-5} g. PbS, 1.25×10^{-6} g. HgS, 3.4×10^{-5} g. CuS, and 1.3×10^{-4} g. CdS. For these same substances, the values given in this book are, 3.3×10^{-9} g. ZnS, 3.3×10^{-5} g. MnS, 7×10^{-10} g. NiS, 7×10^{-10} g. CoS, 3×10^{-7} g. FeS, 3×10^{-7} g. Fe_2S_3,

1×10^{-13} g. Ag_2S, 4.9×10^{-11} g. PbS, 4.6×10^{-26} g. HgS, 8.8×10^{-20} g. CuS and 8.6×10^{-12} g. CdS. These latter values were computed, for the most part, from values given in Landolt-Börnstein and represent fairly well the behavior of the cations in question toward hydrogen sulfide. According to the Fresenius table, silver sulfide is about ten times as insoluble as mercuric sulfide and lead sulfide is one hundred times as insoluble as cadmium sulfide. According to Landolt and Börnstein, mercury sulfide is about a million times as insoluble as copper sulfide.

Owing to the colloidal nature of each of these sulfide precipitates, it is extremely difficult to determine the true solubility and the values are so small that ordinary methods of measurement will not serve. When shaken with water, colloidal solutions of all these substances can be obtained and sometimes, as in the case of copper sulfide, a little sulfate is formed by atmospheric oxidation. The data given for these solubilities in the German text cited, doubtless represent many hours of careful, accurate and skillful analytical work, but, in the case of the sulfide values, there is evidently something wrong if one authority gives the value 1.25×10^{-6} for mercuric sulfide and another authority the value 4.6×10^{-26}. The smaller value, however, alone explains why mercuric sulfide is precipitated from strongly acid solutions and why it does not dissolve appreciably in concentrated hydrochloric acid or in hot nitric acid.

SUBSTANCES SOLUBLE IN WATER

Of Group I (p. 304) the following are soluble:

1. **Chlorides.** — All except **AgCl**, **Cu_2Cl_2**, **Hg_2Cl_2**, **$PtCl_2$**, **AuCl**, **BiOCl**, **SbOCl**, **Mg_2OCl_2**. **$PbCl_2$** and **TlCl** are difficultly soluble.

2. **Bromides.** — The same as the chlorides.

3. **Iodides.** — All except **AgI**, **Hg_2I_2**, **HgI_2**, **Cu_2I_2**, **PdI_2**, **TlI**; **PbI_2** is very difficultly soluble.

4. **Cyanides.** — Only the cyanides of the alkalies, alkaline earths, and mercury.

5. **Ferrocyanides.** — Only those of the alkalies and alkaline earths.

6. **Ferricyanides.** — Same as the ferrocyanides.

7. **Cobalticyanides.** — Only those of the alkalies, alkaline earths, and the ferric, mercuric, and lead salts.

8. **Thiocyanates.** — Those of the alkalies, alkaline earths, iron, cupric copper, and mercuric mercury.

9. **Hypochlorates.** — All.

Of Group II (p. 304) the following are soluble:

10. **Nitrites.** — All. Silver nitrite is difficultly soluble.

11. **Acetates.** — Silver and mercurous acetates and certain basic acetates are difficultly soluble.

12. **Cyanates.** — Those of the alkalies, alkaline earths, and most of the remaining ones. Silver and lead cyanates are insoluble.

13. **Sulfides.** — Only those of the alkalies and alkaline earths. CaS is difficultly soluble.

14. **Hypophosphites.** — All.

Of Group III (p. 304) the following are soluble:

15. **Sulfites.** — Those of the alkalies, and the bisulfites of the alkaline earths.

16. **Carbonates.** — Those of the alkalies, and the bicarbonates of Ca, Sr, Ba, Mg, Fe, Mn.

17. **Oxalates.** — Those of the alkalies; the remainder are difficultly soluble or insoluble. Most oxalates, however, with the exception of Ba, Ca, and Sr oxalates, form soluble complex salts with alkali oxalates.

18. **Iodates.** — Only those of the alkalies.

19. **Borates.** — Those of the alkalies. The remaining borates are all difficultly soluble in water, but soluble in ammonium chloride as a rule.

20. **Molybdates.** — Only those of the alkalies.

21. **Selenites.** — Those of the alkalies are readily soluble, the remaining ones are difficultly soluble.

22. **Selenates.** — All except the barium and lead salts.

23. **Tellurites.** — Only those of the alkalies.

24. **Tellurates.** — Only those of the alkalies.

25. **Tartrates.** — The normal tartrates of the alkalies, and lithium and sodium bitartrates. The remaining tartrates are insoluble in water, but are usually soluble in an excess of alkali tartrate solution, forming complex salts.

26. **Citrates.** — Only those of the alkalies are readily soluble in water. The insoluble citrates usually dissolve in an excess of alkali citrate solution.

27. **Pyrophosphates.** — Only those of the alkalies.

28. **Metaphosphates.** — Only those of the alkalies.

Of Group IV (p. 304) the following are soluble:

29. **Phosphates.** — Only those of the alkalies.

30. **Arsenites.** — Only those of the alkalies.

31. **Arsenates.** — Only those of the alkalies.

32. **Thiosulfates.** — Almost all are soluble, though the silver and barium salts are difficultly soluble.

33. **Chromates.** — Those of the alkalies, Ca, Sr, Mg, Zn, Mn, Fe, and Cu are soluble, the others are difficultly soluble or insoluble.

34. **Vanadates.** — The orthovanadates are unstable; the pyro-, meta-, and polyvanadates are soluble in water, as a rule. The lead and mercurous salts are insoluble, also the vanadates of the iron group.

35. **Periodates.** — All more or less soluble in water, except silver periodate, which is insoluble.

Of Group V (p. 305), the following are soluble:

36. **Nitrates.** — All except a few basic salts.

37. **Chlorates.** — All.

38. **Perchlorates.** — All.

39. **Manganates and Permanganates.** — All.

Of Group VI (p. 305), the following are soluble:

40. **Sulfates.** — All except the Ca, Ba, Sr, and Pb salts, and a few basic sulfates.

41. **Fluorides.** — Those of the alkalies, silver, and mercury; the remaining fluorides are difficultly soluble or insoluble in water.

Of Group VII (p. 305), the following are soluble:

42. **Silicates.** — Only those of the alkalies.

43. **Tungstates.** — Only those of the alkalies.

Of the salts insoluble in water, all dissolve in acid (hydrochloric or nitric) except AgCl, AgBr, AgI, AgCN, AuCl, $PtCl_2$, $BaSO_4$, $SrSO_4$, $PbSO_4$, HgS, Prussian blue, CaF_2, SnS_2 (mosaic gold), SiO_2, many silicates, fused $PbCrO_4$, and the strongly ignited oxides: Al_2O_3, Cr_2O_3, TiO_2, SnO_2, Sb_2O_3.* TiO_2, SnO_2, and Sb_2O_3 can be dissolved by long continued boiling with concentrated hydrochloric acid.

Of the salts insoluble in acids, the following dissolve in aqua regia: $PtCl_2$, AuCl, HgS, Sb_2O_3, SnS_2, and Prussian blue (after long treatment).

The following substances are not dissolved by aqua regia: AgCl, AgBr, AgI, AgCN, $BaSO_4$, $SrSO_4$, $PbSO_4$, CaF_2,† fused $PbCrO_4$, Al_2O_3, Cr_2O_3, native TiO_2 (rutile, anatase, brookite), native SnO_2 (cassiterite, tinstone), SiO_2, Si, many silicates, C, carborundum, and strongly ignited iridium (rhodium, ruthenium, and osmium).

In order to bring such substances in solution it is necessary to subject them to a special treatment. The process to be chosen depends largely upon the nature of the insoluble substance, so that a few general tests are necessary before going farther. Very often the preliminary examination will have been sufficient, but it is always well to perform the following simple experiments:

1. Heat a small portion of the residue insoluble in acids on the charcoal stick to see whether a metallic button can be produced.

(*a*) No metallic button is produced. The *absence* of **silver, lead,** and **tin** is thereby assured.

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* The oxides of antimony are changed to Sb_2O_4 after long ignition in the air.

† Calcium fluoride will be dissolved by the long-continued action of aqua regia.

(*b*) A metallic button is formed. The button is flattened in an agate mortar, and its solubility in acids is tested.

(α) The metal dissolves in nitric acid forming a clear solution, showing the *absence* of **tin.** Add a little hydrochloric acid to the nitric acid solution; a curdy precipitate is formed if the metal is **silver,** consisting of silver chloride, insoluble in water, but soluble in ammonia.

If the nitric acid solution becomes turbid on the addition of sulfuric acid, **lead** is present.

(β) The metal does not dissolve in nitric acid forming a clear solution, but leaves a white, insoluble powder: **metastannic acid.** Treat a new button with concentrated hydrochloric acid, when it will dissolve completely if silver is absent. Mercuric chloride produces a white precipitate of mercurous chloride in the hydrochloric acid solution: tin is present.

2. Heat a second portion of the insoluble residue in a small test-tube with concentrated sulfuric acid and test to see whether the escaping gas renders a drop of water turbid.

A turbidity shows the presence of an insoluble fluoride (CaF_2).

3. Heat another portion of the residue (with the help of a platinum wire) in the upper reducing flame of the gas-burner, allow to cool in the inner mantle, moisten with dilute hydrochloric acid, and notice whether the odor of hydrogen sulfide can be detected. Then test to see whether it will now impart a characteristic coloration to the flame. The presence of a sulfate is betrayed by the odor of hydrogen sulfide, and the flame test shows whether barium alone or a mixture of barium, calcium, and strontium is present.

4. Test another portion of the residue in the salt of phosphorus bead; silicic acid or a silicate usually gives a skeleton bead (cf. p. 446).

As the skeleton bead is not always obtained even when silica is present, a further test for silicic acid is often necessary (cf. p. 445).

5. Now heat the salt of phosphorus bead in the reducing flame to test for the presence of **titanium,** which causes the bead to become violet. The violet color appears more quickly on the addition of a little piece of tin-foil. If iron is present at the same time, as is always true in the case of rutile, the bead is colored brownish red in the reducing flame.

6. The presence of **chromium** is often detected by the green color of the residue. In the case of chromite (gray or black residue) fuse some of the substance with sodium carbonate and potassium nitrate in the loop of a platinum wire (cf. p. 149), when a yellow melt is obtained if **chromium** is present, which (after being dissolved in water and

acidified with acetic acid) yields, with silver nitrate, a reddish-brown precipitate of silver chromate.

7. If the residue is gray or black, it may also consist of **carbon.** Heat a small portion upon a piece of platinum-foil; if carbon is present, the mass will glow and, if it does not burn completely, a lighter-colored ash will be obtained. In doubtful cases melt a little potassium chlorate in a test-tube, and add a little of the insoluble residue; a distinct glowing or a little explosion will take place if carbon is present. It is necessary to avoid the addition of shreds of filter-paper in this test.

8. **Silicon** and **Silicides** (carborundum, etc.) are seldom met with, and show the greatest stability toward the above-mentioned reagents. By fusing with caustic alkali in a silver crucible, however, they are readily decomposed with evolution of hydrogen (cf. p. 447).

After dissolving the melt in water and acidifying, gelatinous silicic acid separates out, particularly after evaporation.

Methods for Getting Substances into Solution which are Insoluble in All Acids

1. **Insoluble Halogen Compounds** (the silver compounds alone come into consideration) can be brought into solution by melting the mass, adding a little dilute sulfuric acid and a piece of zinc so that it comes in contact with both the acid and the insoluble substance. After a while pour off the acid; it contains the halogen acid in the presence of zinc sulfate, and should be kept for the subsequent tests for acids, cf. p. 326. The residue consists of metallic silver. Wash it with water, dissolve in dilute nitric acid, filter and test the solution for silver with hydrochloric acid.

2. **Insoluble Sulfates of the Alkaline Earths** are brought into solution by fusing in a platinum crucible with four to five times as much calcined sodium carbonate, or with a mixture of equal parts of sodium and potassium carbonates. Mix the finely powdered substance in the crucible with the sodium carbonate, cover the mixture with a thin layer of more carbonate, place the lid on the crucible and heat at first gently over a small flame in order to drive off the moisture which the carbonate always contains, and then raise the temperature until the mass fuses to a thin liquid; maintain this temperature for about fifteen minutes. Remove the fused mass from the crucible as directed on p. 445. Heat with a little water on the water bath until the fused mass disintegrates, and no more hard lumps can be felt with a glass rod, then filter. The filtrate will contain the sulfate

as sodium sulfate, and the residue will consist of carbonates of the alkaline earths. Wash it with a 5 per cent sodium carbonate solution until no more sulfuric acid can be detected in the filtrate, and then wash with hot water until the wash-water no longer reacts alkaline (cf. p. 116). Dissolve the residue in acid, and analyze as described on p. 118, 120 or 122.

Although it would take repeated treatments to effect the complete decomposition of even a relatively small quantity of barium sulfate, any sulfate can be decomposed sufficiently to obtain qualitative tests for cation and ion by merely boiling the finely-powdered substance with 3-normal sodium carbonate solution. Thus boiling 1 g. of powdered barium sulfate with 25 cc. of 3-normal sodium carbonate serves to convert about 80 per cent of the insoluble sulfate into insoluble carbonate and water-soluble sulfate:

$$BaSO_4 + Na_2CO_3 \rightarrow BaCO_3 + Na_2SO_4.$$

After washing thoroughly to remove the sulfate, about 80 per cent of the residue will dissolve in dilute acid. The decomposition of the sulfates of lead, calcium, and strontium (also bismuth) is practically complete by this treatment.

3. **Lead Sulfate** may be boiled with a concentrated sodium carbonate solution, which forms insoluble basic lead carbonate and soluble sodium sulfate; with caustic soda, which forms soluble lead plumbite and sodium sulfate; or with ammonium acetate (cf. p. 222).

4. **Silicic Acid** and **Silicates** should be fused with sodium carbonate, exactly as described on p. 445, or treated with sulfuric and hydrofluoric acids as described on page 446.

5. **Metastannic Acid**, as obtained by the oxidation of tin with nitric acid, is readily dissolved by boiling with a little concentrated hydrochloric acid, and then treating with considerable cold water (cf. p. 273).

Tin dioxide, as it occurs in nature (tinstone), as well as the strongly ignited metastannic acid, cannot be brought into solution in this way. One of the methods mentioned on p. 277 (usually the sodium carbonate and sulfur method) must be used.

6. **Insoluble Fluorides** are first heated with concentrated sulfuric acid in platinum and any alkaline earth sulfate formed is brought into solution by the method described under 2.

7. **Titanium Dioxide** is fused with potassium pyrosulfate in a platinum crucible (cf. pp. 138 and 165); or it is fused with sodium carbonate, the melt treated with cold water, and the residue dissolved in hydrochloric acid (cf. p. 166). Heating for some time with concentrated sulfuric acid will dissolve pure titanium dioxide. When cold the solution may be diluted.

Fusion with potassium pyrosulfate is also suitable for decomposing native aluminium oxide (corundum).

8. **Chromium Trioxide** and **Chromite** are fused with sodium carbonate and a little potassium nitrate in a platinum crucible or with sodium peroxide in a nickel or iron crucible (cf. p. 142).

9. **The Insoluble Complex Cyanides** are completely decomposed by boiling with caustic soda in a porcelain dish.

After boiling with the alkali, dilute with water and filter. The filtrate will contain the acid in the form of its sodium salt; and, in some cases, may also contain aluminium and zinc. Saturate the filtrate with carbon dioxide, boil and filter off any precipitate ($Al(OH)_3$ or $ZnCO_3$); dissolve this precipitate in hydrochloric acid and test for zinc and aluminium. Acidify the alkaline filtrate obtained above with hydrochloric acid and test for ferrocyanic and ferricyanic acids according to pp. 338 and 341.

The soluble complex cyanides are decomposed before the analysis by heating them with concentrated sulfuric acid (cf. p. 161).

REACTIONS THAT ACCOMPANY THE DISSOLVING PROCESS

When a substance is dissolved, whether in water or in acids, phenomena are often observed which may be of great importance as concerns the subsequent analysis. Moreover, the color, reaction of the solution towards indicators, or the evolution of gases will lead to important conclusions. First, test the substance with regard to its solubility in water, by taking about 0.5 gm. of the fine powder, adding a little cold water, and noting whether any bubbles of gas are given off.

A gas is evolved when there are present:

(*a*) **Peroxides of the Alkalies** or **Alkaline Earths**, which are partly decomposed into hydroxide and oxygen:

$$2\,\mathbf{Na_2O_2} + 2\,H_2O = 4\,NaOH + O_2\uparrow;$$

$$2\,\mathbf{BaO_2} + 2\,H_2O = 2\,Ba(OH)_2 + O_2\uparrow.$$

Barium peroxide is decomposed in this way only by heating the water.

Test the escaping gas for oxygen by means of a glowing splinter.

In the alkaline solution (red litmus is changed to blue) some undecomposed peroxide will still be found.

Dilute the solution with considerable water, cool, and carefully acidify with sulfuric acid, add a little ether, some potassium dichromate solution, and shake the mixture. If a peroxide is present, the upper ether layer will now be colored blue. A better method for detecting the hydrogen peroxide, formed by the action of the sulfuric acid upon the peroxide, consists in adding a few drops of titanium sulfate solution; a distinct yellow color will be noticed if only traces of hydrogen peroxide are present (cf. pp. 88 and 168).

(*b*) **Carbides of the Alkaline Earths** (calcium carbide).

These are decomposed into acetylene (which has a peculiar odor, and burns with a luminous flame) and calcium hydroxide:

$$CaC_2 + 2\,H_2O = Ca(OH)_2 + C_2H_2\uparrow.$$

(*c*) **Nitrides of the Alkaline Earths** (magnesium nitride).

Magnesium nitride is decomposed by water into magnesium hydroxide and ammonia:

$$Mg_3N_2 + 6\,HOH = 3\,Mg(OH)_2 + 2\,NH_3\uparrow.$$

If considerable water is added, there is no gas evolution, because the ammonia will be dissolved by the water; but on boiling the solution, ammonia will be given off, which can be readily recognized by its odor.

(*d*) **Phosphides of the Alkalies and Alkaline Earths.** — These are decomposed by water, setting free spontaneously combustible phosphine:

$$Ca_2P_2 + 4\,H_2O = P_2H_4\uparrow + 2\,Ca(OH)_2.$$

Very small quantities of the phosphide can be recognized by the characteristic garlic odor.

(*e*) **Many Chlorides, Bromides,** and **Iodides of the Negative Elements,** e.g., PCl_3, PCl_5, etc., are decomposed into the halogen hydride and the oxygen acid of the negative element:

$$PCl_5 + 4\,H_2O = 5\,HCl + H_3PO_4.$$

(*f*) **A Few Sulfides which are Seldom Encountered** (MgS, Al_2S_3, etc.). — These are decomposed by water with loss of hydrogen sulfide, which can be detected by its odor, and by its blackening lead acetate paper:

$$MgS + 2\,H_2O = Mg(OH)_2 + H_2S\uparrow.$$

After any reaction caused by the first addition of water is over, add about 10 to 15 cc. more, heat the water to boiling and then allow it to cool.

If the substance dissolves completely, forming a clear solution, it is evident that it is unnecessary to test for any insoluble substances in the subsequent analysis.

If a residue remains, it is possible that a part of the substance has dissolved in the water. To determine whether this is the case, decant the liquid through a filter and carefully evaporate a little of the filtrate to dryness on platinum-foil (or a watch-glass). If the foil is heated too hot, volatile compounds may escape unnoticed. If a residue remains after evaporation, it is evident that a part of the original substance is soluble in water. Then treat the original residue

several times with small quantities of water, and analyze the aqueous extract thus obtained by itself. Treat the part remaining undissolved with acid, using hydrochloric acid unless the preliminary examination has shown the presence of either lead or silver, when nitric acid should be used.

Treat the residue with 0.5–1 cc. of 12-normal acid (notice whether there is any evolution of a gas), heat gently, and then dilute with water, to dissolve any chlorides insoluble in hydrochloric acid. It must be remembered, however, that bismuth and antimony salts form insoluble basic chlorides on dilution with water, so that too much water should not be added.

If a residue remains after treatment with acid, bring it into solution by one of the methods described on pp. 466–8.

II. Examination for the Metals (Cations)

TABLE XVI. — GENERAL SCHEME FOR SEPARATING THE METALS INTO GROUPS

Solution may contain all the common basic constituents. *Add HCl in slight excess.* (1)

Precipitate: Group I. *Examine as outlined in Table XV, p. 302.* (2)	Filtrate: Groups II, III, IV and V. *Saturate with H_2S.* (3)			
	Precipitate: Group II. *Examine as outlined in Table IX, p. 289, or Table XII, p. 294.* (4)	Filtrate: Groups III, IV and V. Test for phosphoric acid. If found present modify the following procedure as indicated in Table XVII. *Add NH_4OH and $(NH_4)_2S$.* (5)		
		Precipitate: Group III. *If phosphate is absent examine as outlined in Table VII, p. 199, or in Table VIII, p. 203. If phosphate is present examine by Table XVII, p. 475.* (6)	Filtrate: Groups IV and V. *Add $(NH_4)_2CO_3$.* (7)	
			Precipitate: Group IV. *Examine as outlined in Table IV, p. 118, or in Table V, p. 120, or in Table VI, p. 122.* (8)	Filtrate: Group V. *Examine as outlined in Table I, p. 101, or in Table II, p. 104, or Table III, p. 105.* (9)

PROCEDURE

1. Add HCl as directed on p. 303. If the original substance was completely soluble in dilute HCl, it is evident that no silver or mercurous salt is present. Often, when lead is present, the solution is clear while hot, but lead chloride is deposited as the solution cools. It is usually best to filter off such a precipitate, but it will be

changed to less soluble lead sulfide when H_2S is introduced to precipitate the second group. If the original solution is alkaline to phenolphthalein or to litmus, a precipitate may form when none of the metals of the first group is present. Thus a solution of sodium silicate gives a white, gelatinous precipitate of silicic acid, a solution of an alkali tungstate gives a precipitate of tungstic acid, a solution of a thio salt of arsenic, antimony or tin gives a colored sulfide precipitate and the solution of a complex cyanide may form a precipitate when neutralized. These precipitates, however, are not likely to be mistaken for a chloride of silver, lead or mercury. If a silicate is present, it is absolutely necessary to remove the silicic acid at the start by the method given on p. 444 and tungstic acid may be removed in exactly the same way. If a thio salt is present, examine the precipitate according to Table XI, p. 292, and test for alkalies and alkaline earths according to Table IV, p. 118, and Table I, p. 101. If the original solution is alkaline, it is necessary to test for iron and aluminium only when the solution contains non-volatile organic matter which prevents the precipitation of these elements by hydroxyl ions. The addition of HCl may cause the precipitation of BiOCl and dilution may cause the precipitation of BiOCl, SbOCl or a basic salt of some other metal, especially titanium and tin. With the exception of the titanium precipitate, such basic salts are easily dissolved by filtering and treating with 6-normal HCl, or the basic salts of antimony, bismuth and tin may be changed into less soluble sulfides by introducing H_2S without filtering.

2. Examine the precipitate of Hg_2Cl_2, $PbCl_2$ and AgCl exactly as described on p. 302. For the detection of thallium, which is sometimes precipitated with this group, consult Part V.

3. Transfer the filtrate from (1) to a 300-cc. Erlenmeyer flask, fit the latter with a two-holed rubber stopper and insert through one hole a right-angled glass tube which reaches nearly to the bottom of the flask and through the other hole a shorter tube, similarly bent, which reaches only to the bottom of the rubber stopper. Raise the longer tube till it is just above the surface of the solution, heat the solution to boiling and begin passing a steady stream of H_2S through the longer tube. Remove the flame from beneath the flask, close the shorter tube with a piece of rubber tubing which has one end stopped up with a short piece of stirring rod, and lower the longer tube so that it dips well below the surface of the solution. Shake well and continue keeping up the pressure of the H_2S; in this way the gas is absorbed as fast as the sulfide precipitates and the solution is kept saturated with the gas without wasting a great deal of it. When the precipitation appears to be complete, shut off the H_2S, open the flask, add an equal volume of cold water and again saturate with H_2S. Close the short tube and shake the flask well for two or three minutes while keeping up the H_2S pressure. Finally filter off the precipitate and wash it promptly with H_2S water. If an oxidizing agent is present,* considerable free sulfur will be deposited and this will greatly delay the precipitation of the sulfides. In case it is desired to know whether a precipitate contains nothing but sulfur, wash it several times with alcohol, then with carbon disulfide (away from any free flame) and then with alcohol again; this treatment will serve to remove the sulfur. It is important to adjust the concentration of the acid properly before introducing H_2S by measuring the quan-

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* If much oxidizing agent or considerable arsenic acid is present, it is best to pass SO_2 into the hot solution until a complete reduction is accomplished and then remove the excess of SO_2 by a stream of CO_2. If the excess of SO_2 is not removed, it reacts with H_2S chiefly as follows: $2\,H_2S + SO_2 \rightarrow 2\,H_2O + 3\,S$.

tity added in getting the substance into solution and in precipitating the first group. After diluting with water, as above directed, the solution should be about 0.3-normal in acid; if more acid is present cadmium and lead sulfides will not precipitate and if less acid is present sulfides of zinc, nickel and cobalt may precipitate. On the whole it is better to err with too little acid rather than with too much, as enough zinc, nickel and cobalt will always remain in the filtrate to give a test in the next group and the presence of these elements does not seriously interfere with the analysis of the second group. Like cadmium, zinc gives a white ferrocyanide in the confirmatory test for copper, and nickel gives a faint blue with ammonia; either nickel or cobalt will interfere with the final test for cadmium, but the treatment outlined on p. 292 will overcome this difficulty. If after precipitating with hydrogen sulfide a turbid filtrate is obtained, due to free sulfur, prepare some filter-paper pulp by shaking pieces of filter paper in a bottle with hot water, add some of the pulp to the filtrate and filter through a fresh filter. The hydrogen sulfide precipitate oxidizes somewhat on being exposed to the air, and a little soluble sulfate is likely to form which forms a precipitate on coming in contact with H_2S in the filtrate. For this reason the precipitate should be washed promptly with hydrogen sulfide water without ever letting the filter drain completely until the washing is finished. If the filter clogs, place the filter and precipitate in a beaker, shake it up with hydrogen sulfide water and filter through a fresh filter. In qualitative analysis, all but the first washings of a precipitate should be discarded, as a rule.

4. Examine the hydrogen sulfide precipitate as directed on p. 290 or 294. If gold, platinum or considerable tin is present, these elements are often found in the residue of mercuric sulfide obtained after treatment with nitric acid. When the presence of these elements is suspected, take a little of the residue for the mercury test and fuse the remainder in a *porcelain* crucible with a mixture of equal parts potassium cyanide and sodium carbonate. Cool, wash out all the soluble alkali salts with water and discard this solution. Gold, platinum, tin and lead will be left behind in the metallic condition. Treat the metallic residue with dilute nitric acid and test the solution for lead in the regular way with sulfuric acid (p. 290). Heat the residue of gold, platinum and metastannic acid with concentrated hydrochloric acid. Dilute, filter and test for tin with $HgCl_2$ in the usual way (p. 293). Dissolve any gold or platinum in aqua regia, add ammonium chloride, evaporate to dryness on the water bath and treat the residue with a very little water; a yellow precipitate of $(NH_4)_2[PtCl_6]$ shows the presence of platinum. Filter, test with $FeSO_4$ for gold, and confirm by the charcoal stick reaction (p. 283).

5. Take a little of the filtrate from (3), boil off the hydrogen sulfide, add a little bromine water to oxidize any iron and the last traces of hydrogen sulfide and make alkaline with ammonia. If a precipitate forms it may consist of a phosphate of barium, strontium, calcium or magnesium, or an alkaline earth fluoride or oxalate. Phosphoric acid very often occurs in minerals, and for this reason a special procedure is often required for the analysis of Groups III and IV. Without stopping to filter off the precipitate produced by ammonia, dissolve it by the careful addition of a little nitric acid, heat the solution nearly to boiling and add an equal volume of ammonium molybdate reagent. A yellow precipitate, which may be slow in forming, shows that phosphoric acid is present. Arsenic acid gives a similar precipitate (p. 246), but arsenic should not be present at this stage in the analysis. If phosphoric acid is found present, examine the precipitate as outlined in Table XVII. If an oxalate or fluoride is indicated by the preliminary examination, especially by the test with concentrated sulfuric acid, it is best to remove these acids by heat-

ing the original substance with concentrated sulfuric acid. This is likely to leave, after diluting, an insoluble residue of alkaline earth sulfate which should be examined as directed on p. 466. If the behavior of the original substance in the closed tube test indicated the presence of non-volatile organic matter, it is necessary to remove it before proceeding with the analysis of Group III, because tartaric and citric acids, sugars, starches and similar substances prevent the precipitation of iron, aluminium and chromium with ammonia. Such organic substances can be removed by ignition or by repeated treatment with concentrated sulfuric and nitric acids; add about 5 cc. of sulfuric acid, an equal volume of concentrated nitric acid and evaporate till strong fumes of sulfuric acid are evolved, cool and repeat the treatment with nitric acid as much as necessary. The ignition treatment often makes Al_2O_3, Cr_2O_3, Fe_2O_3 and SiO_2 insoluble. Fuse such a residue with $KHSO_4$ and examine it by itself. The treatment with sulfuric and nitric acid is likely to leave an insoluble sulfate behind; fuse it with sodium carbonate (p. 116).

6. If phosphate is found present, analyze as outlined in Table XVII, p. 475. If phosphate is absent, analyze Group III by method A, p. 199, or by method B, p. 203. Many of the elements in this group commonly occur in different states of oxidation. In reporting the final results of the analysis it is not sufficient to state that iron, chromium, or manganese is present, but it should be stated in what condition such an element is present in the sample as received. It is necessary to determine this by special tests, using the characteristic reactions described in Part II under the element in question.

7. Treat the filtrate from (5) with $(NH_4)_2CO_3$ according to Method A, p. 118, or according to Method B, p. 120. In the former case magnesium will not be precipitated with this group and in the latter case it will be precipitated. In most cases, Method B will be found preferable.

8. Examine the $(NH_4)_2CO_3$ precipitate as directed on p. 118 or as directed on p. 120.

9. Examine the alkali group according to the directions on p. 101 or on p. 104, omitting the magnesium test provided Method B was used for the analysis of Group IV. Test a portion of the original substance for ammonium.

ANALYSIS IN THE PRESENCE OF PHOSPHORIC ACID

There are three classic methods for examining a solution for the members of Groups III and IV when phosphoric acid is present. The first of these methods depends upon the fact that when tin is boiled with strong nitric acid, insoluble metastannic acid is formed (p. 273) and this precipitate carries down with it phosphoric acid, arsenic acid and to a lesser extent other substances such as ferric oxide, titanium oxide, etc. It is probable that adsorption compounds are formed, rather than simple chemical compounds. Instead of using metallic tin, it has been found possible to accomplish the same result by preparing metastannic acid in advance and adding it to the solution.* After the phosphoric acid has been precipitated in this way, it is filtered off and the filtrate examined for Groups III and IV in the usual manner.

The second method of analysis in the presence of phosphoric acid is the so-called *basic acetate method.* If a solution containing ferric iron or aluminium is carefully neutralized, ferric phosphate or aluminium phosphate is precipitated before an insoluble hydroxide or an alkaline earth phosphate is formed. If the neutralization

* Cf. W. MECKLENBURG, *Z. anal. Chem.*, **52**, 293 (1913).

goes too far, and an excess of hydroxyl ions is provided, ferric and aluminium hydroxides are likely to be formed and alkaline earth phosphate will then precipitate. One of the best methods of preventing the neutralization going too far is to boil the dilute solution with a little acetic acid and considerable sodium acetate. Then, if a slight excess of iron is present, all of the phosphoric acid will be precipitated as ferric phosphate and the excess of iron will be precipitated as basic acetate. It is better to use ferric iron rather than aluminium in this separation, because basic ferric acetate by its color shows when enough trivalent metal is present.

The third method of analysis is the *barium carbonate method.* This method is the same in principle as the basic acetate method except that the solution is neutralized with barium carbonate in the cold. The objection to this method of analysis is that an alkaline earth is added so that a separate portion of the solution must be used in the tests for this group. In some special cases calcium carbonate, zinc oxide and cadmium carbonate are used instead of barium carbonate. All of these substances will neutralize a solution sufficiently to precipitate phosphates and hydroxides of iron, aluminium and chromium. They do not, however, precipitate bivalent metals as a soluble carbonate would.

The barium carbonate method is useful for separating the trivalent from the bivalent metals of Group III and will be described in Volume II of this book. The other two methods will be outlined here.

PROCEDURE. TIN METHOD

1. Evaporate the filtrate from Group II just to dryness. Add 10 cc. of concentrated HNO_3, evaporate to dryness and repeat the evaporation with HNO_3 once more. Finally add 10 cc. of concentrated HNO_3 and introduce about 1 gm. of tin foil in small portions. Boil to small volume in order to complete the precipitation of the tin and pour the concentrated solution into 100 cc. of water contained in a narrow cylinder such as a 100-*cc. graduate.* Next morning siphon off the supernatant liquid and discard the precipitate of metastannic acid, which should contain all the phosphoric acid.

2. The tin foil usually contains traces of lead and copper. To remove these, saturate the solution with H_2S and filter. Reject the precipitate.

3. Treat the filtrate with NH_4OH and $(NH_4)_2S$, examine the precipitate for Group III and the filtrate for Groups IV and V exactly as outlined in Table XVI, p. 470.

TABLE XVII. — ANALYSIS OF GROUPS III AND IV IN PRESENCE OF PHOSPHATE

<table>
<tr><td colspan="3">Tin Method.</td><td colspan="3">Basic Acetate Method.</td></tr>
<tr><td colspan="3">Remove H_2S and HCl from filtrate from Group II, and evaporate repeatedly with HNO_3. Add tin foil, concentrate, dilute and allow the precipitate to settle. (1)</td><td colspan="3">Treat filtrate from Group II with NH_4OH and $(NH_4)_2S$. Filter and test filtrate as in Table XVI. Examine the precipitate according to Table VI up to and including treatment with HNO_3 and $KClO_3$. Test for Fe^{+++} in filtrate from MnO_2 precipitate. Add NH_4OH, $HC_2H_3O_2$, $FeCl_3$ and $NH_4C_2H_3O_2$. Dilute and boil. (4)</td></tr>
<tr><td>Precipitate: $(H_2SnO_3)x \cdot (P_2O_5)y$. Reject.</td><td colspan="2">Solution: Groups III, IV and V. Saturate with H_2S and filter. (2)</td><td>Precipitate: $FePO_4$ and $Fe(OH)_2C_2H_3O_2$. Reject.</td><td colspan="2">Filtrate: Ni^{++}, Co^{++}, $(Zn^{++})Ba^{++}$, Sr^{++}, Co^{++}, Mg^{++}. Add NH_4OH and saturate with H_2S. (5)</td></tr>
<tr><td></td><td>Precipitate: CuS, PbS from impurities in tin foil. Reject.</td><td>Solution: Groups III, IV and V. Add NH_4OH and $(NH_4)_2S$ and continue as in Table XVI. (3)</td><td></td><td>Precipitate: CoS, NiS, (ZnS). Examine as in Table VIII.</td><td>Filtrate: Ba^{++}, Sr^{++}, Ca^{++}, Mg^{++}. Examine for Group IV as in Table XVI, but do not test for Group V as Na^+ and K^+ have been added. (6)</td></tr>
</table>

BASIC ACETATE METHOD

4. Treat the filtrate from Group II with NH_4OH and $(NH_4)_2S$ in the usual way. The precipitate may contain FeS, NiS, CoS, ZnS, MnS, $Al(OH)_3$, $AlPO_4$, $Cr(OH)_3$, $CrPO_4$, $Ba_3(PO_4)_2$, $Sr_3(PO_4)_2$, $Ca_3(PO_4)_2$, and $MgNH_4PO_4$. The filtrate may contain Ba^{++}, Sr^{++}, Ca^{++}, Mg^{++}, Na^+, K^+ and NH_4^+. Examine the filtrate for Groups IV and V as in Table XVI. The precipitate must be tested independently for Ba^{++}, Sr^{++}, Ca^{++} and Mg^{++}.

Dissolve the precipitate in HCl, adding a little HNO_3 if necessary. Dilute, filter off any residual sulfur and evaporate the filtrate nearly to dryness to remove the excess acid. Dilute to 20 cc., make alkaline with NaOH and add more water if a very bulky precipitate is formed. Add about 2 cc. of Na_2O_2 powder in small portions while stirring the cold solution. Then add 5 cc. of 4-normal Na_2CO_3 solution and boil to decompose the excess of Na_2O_2. Cool, dilute with an equal volume of water and filter. The filtrate will contain all the aluminium as sodium aluminate, all the chromium as sodium chromate, usually most of the zinc as sodium zincate and some or all of the phosphoric acid as sodium phosphate. Examine this filtrate

for aluminium, chromium and zinc exactly as outlined in Table VIII, p. 203. The presence of the phosphate does no harm, as zinc phosphate is readily soluble in ammoniacal solutions. When the solution which was treated with sodium hydroxide and sodium peroxide contains alkaline earths, the phosphates of these elements are precipitated by the neutralization and if the solution contains no alkaline earth metal, usually most of the phosphate remains in solution. The sodium carbonate is added with the sodium hydroxide and sodium peroxide to ensure the complete precipitation of alkaline earth and to prevent the precipitation of an alkaline earth chromate.

Dissolve the precipitate produced by NaOH, Na_2O_2 and Na_2CO_3 in 15 cc. of 6-normal HNO_3, adding H_2O_2 a few drops at a time until the precipitate is all dissolved. Filter if any filter paper is present and evaporate the filtrate nearly to dryness. Add 16-normal HNO_3 and treat with $KClO_3$ exactly as described on p. 205. If a precipitate of MnO_2 is formed, filter it off and, if deemed necessary, confirm the manganese in the usual way. Take one-tenth of the filtrate from the $KClO_3$ treatment, evaporate it just to dryness, moisten the residue with a few drops of concentrated HCl, dilute with 5 cc. of water and test for iron with KCNS. Neutralize the remainder of the solution with ammonia and continue adding ammonia until a permanent precipitate is formed or the solution becomes alkaline. Dissolve the precipitate in acetic acid, avoiding an excess, and add 15 cc. of 3-normal $NH_4C_2H_3O_2$ solution. If the solution is then of a rich brownish red color, it is evident that more than sufficient iron is present to combine with all the phosphoric acid. Otherwise add $FeCl_3$ solution, drop by drop, until such a color is produced. Dilute to at least 100 cc. and boil for five minutes in a 500-cc. flask. If a large precipitate is formed, dilute to 250 cc. with hot water and boil a minute longer. Allow the precipitate to settle for a minute or two, filter while still hot through a plaited filter and wash the precipitate with hot water containing a little ammonium acetate. Add 10 cc. more of $NH_4C_2H_3O_2$ to the filtrate, again boil and collect any further precipitate on a separate filter. Reject both of these precipitates, which contain all the phosphoric acid as pale-yellow ferric phosphate and the excess of the iron as basic ferric acetate.

5. Make the filtrate ammoniacal and saturate it with H_2S. Filter and examine the precipitate for nickel, cobalt and zinc according to the directions on p. 206.

6. Examine this last filtrate, which may contain Ba++, Sr++, Ca++ and Mg++ for Group IV as outlined in Table XVI, p. 470. Inasmuch as NaOH, Na_2O_2 and $KClO_3$ have been added the original filtrate from the NH_4OH and $(NH_4)_2S$ precipitation must be examined independently for Groups IV and V.

EXAMINATION FOR THE ACID CONSTITUENTS (ANIONS)

METHOD OF F. P. TREADWELL *

The tests for the acid constituents (anions) are usually made after the analysis for the basic constituents (cations); the preliminary examination (heating in the closed tube and with dilute and concentrated sulfuric acid) and the solubility, combined with the knowledge of the metals that are present, indicate what acids may and what acids may not be present.

* Based on Bunsen's classification of the acids (cf. p. 304.)

In order to avoid side-reactions, the acids are usually obtained in the form of the neutral alkali salts before proceeding to test for them.

PREPARATION OF THE SOLUTION FOR THE ANALYSIS FOR ACIDS

Two cases may be distinguished:

A. The original substance contains no heavy metal (i.e., only alkalies or alkaline earths are present).

(*a*) **The substance is soluble in water.**

Test the solution with litmus paper to see whether it is acid, alkaline, or neutral.

An Alkaline Reaction shows the possible presence of alkali cyanides, alkali nitrites,* borates, tertiary phosphates, alkali sulfides, thio salts of the alkalies, alkali silicates, etc.

An Acid Reaction is shown by many acid salts (cf. p. 50).

Divide the solution into two parts. If it is neutral, analyze it directly for the acids; if it is alkaline, neutralize † half of it with acetic acid and the other half with nitric acid; if it is acid, neutralize with sodium carbonate solution.

(*b*) **The substance is insoluble or very difficultly soluble in water,** but readily soluble in dilute acids. In this case only the acids of Groups III and IV need be tested for.

Boil the dry substance with a little concentrated sodium carbonate solution and filter. The filtrate contains the acids in the form of their sodium salts.

Neutralize the solution with dilute nitric acid.

(*c*) **The substance is insoluble in water and in dilute acids.**

The following substances may be present: $BaSO_4$, $SrSO_4$, ($CaSO_4$), CaF_2, and silicates, which often contain salts of H_3PO_4, HBO_2, H_2SO_4, HF, and HCl.

Fuse the substance with sodium carbonate in a platinum crucible, extract with water, and use the aqueous solution thus obtained for the analysis for acids, after neutralizing.

If the substance is partly soluble in water and in acids, first treat with water and then with sodium carbonate solution and fuse the residue with solid sodium carbonate. Analyze separately the three solutions thus obtained.

B. The substance contains heavy metals.

(*a*) **It is Soluble in Water** or in dilute acids, and contains no non-volatile organic matter (no carbonization in the closed-tube test.)

Treat the solid substance with sufficient concentrated sodium carbonate solution to make the resulting solution weakly alkaline, and filter. If ammonium salts are present, first boil it with the solution of sodium carbonate until the vapors from the solution no longer smell of ammonia, and then filter.

Divide the resulting solution into two parts, making one part acid with acetic acid, and the other with nitric acid.

(*b*) **The Substance is Soluble in Water or Dilute Acids and Contains Non-volatile Organic Matter.** — If the metals of the ammonium sulfide and hydrogen sulfide groups are both present, pass hydrogen sulfide into the weakly acid solution until

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* Perfectly pure alkali nitrites are neutral. The alkaline reaction of the commercial salts is due to the presence of alkali oxide or silicate.

† Thio salts, silicates, stannites, stannates, aluminates, molybdates, tungstates, etc., will yield precipitates at this point which should be examined as described" on page 471.

it is saturated, filter off the precipitate, add ammonia to the filtrate until it is slightly alkaline, filter again, and make this last filtrate acid with acetic acid and evaporate to a small volume. Filter off the deposited sulfur, treat the solution with solid potassium carbonate, filter if necessary, carefully acidify with nitric acid, stir vigorously, and if any potassium acid tartrate is formed, filter it off and test as described on p. 387. Test the filtrate for the remaining acids.

(*c*) **The Substance is Insoluble in Strong Acids.** — Besides the salts mentioned under *A* (*c*), the following may be present: AgCl, AgBr, AgI, AgCN, $PbSO_4$, silicates (ferro- and ferricyanides).

If silver is present, the halogen acids must be looked for. Reduce the insoluble silver salt by zinc and sulfuric acid, filter off the residue, and examine the filtrate according to Table XX for HCl, HI, HBr, and HCN.

If the insoluble substance contains lead, boil it with sodium carbonate solution and filter; make the filtrate acid with hydrochloric acid, and test with $BaCl_2$ for H_2SO_4.

If silicates are present, H_3PO_4, HF, HBO_2, HCl, and H_2SO_4 must also be tested for.

In whatever way a solution is prepared, determine its behavior toward **silver nitrate** and **barium chloride** in order to ascertain to what groups the acids present belong.

Then make the necessary tests for the individual members.

TABLE XVIII. — THE SILVER NITRATE TEST

Treat the original, neutral, aqueous solution, or the solution which has been neutralized with acetic or nitric acid, with an excess of silver nitrate.

No Precipitate is Formed.

All acids of Groups I, III, and IV are absent (cf. p. 304).

A Precipitate is Formed.

If the solution was very concentrated, the precipitate may be the silver salt of $HC_2H_3O_2$, HNO_2, or H_2SO_4. *Add water and heat.*

The Precipitate Dissolves.

All acids of Groups I, III, and IV are absent.

The Precipitate Remains Undissolved.

Acids of Groups I, III, and IV may be present. *Heat the precipitate with dilute nitric acid.*

The Precipitate Dissolves.

One or more acids of Groups III and IV is present. The acids of Group I are absent.

The Precipitate Does not Dissolve.

Present: Acids of Group I.

Filter off the precipitate and treat the filtrate drop by drop with dilute ammonia.

A Turbid Zone is Formed.

Present: Groups* III or IV.
Yellow zone. Ag_3AsO_3. Ag_2PO_4,
Red " Ag_2CrO_4,
Brown " Ag_3AsO_4,†
White " silver salts of H_2SO_3. $H_2C_4H_4O_6$. $H_2C_2O_4$. HPO_3, $H_4P_2O_7$.

No Turbid Zone is Formed.

Absent: Groups III and IV.

* Boric acid would not be precipitated in case the free acid was neutralized with ammonia. It must be tested for separately.

† It must not be forgotten that NH_4OH sometimes produces a brownish precipitate of Ag_2O in silver solutions; in case the zone appears brown, shake the solution gently which will cause the turbidity to disappear; add more NH_4OH, and with a little experience it can be determined whether the turbidity is Ag_2O or Ag_3AsO_4.

TABLE XIX. — THE BARIUM CHLORIDE TEST

Treat the original aqueous, neutral solution, or the solution neutralized with acetic acid, with an excess of barium chloride solution.

No Precipitate is Formed.	A Precipitate is Formed.		
Absent: All acids of Groups III, IV, and VI.	*Add a little dilute HCl and heat the solution.**		
	The Precipitate Dissolves.	The Precipitate Remains.	
	Absent: Group VI (H_2SO_4 and HF).	Present: Group VI.	
		Filter off the precipitate and neutralize the filtrate with pure KOH or NaOH (free from carbonate, etc.).	
		No Precipitate is Formed.	A Precipitate is Formed.
		Absent: Acids of Groups III and IV.	Present: Acids of Groups III and IV.

* Carbonates, sulfites, and thiosulfates will be destroyed; they must afterwards be tested for specially.

TABLE XX. — EXAMINATION OF GROUP I

*First test for HCN by placing a little of the solution on a watch-glass, adding a few drops of yellow ammonium sulfide, evaporating carefully to dryness, acidifying the dry mass with HCl, and adding a drop of $FeCl_3$ solution. If a blood-red coloration is produced, HCN is present, in which case treat a larger portion of the neutral solution with nickel sulfate * solution in excess, and filter.*

PRECIPITATE.	SOLUTION.	
$Ni(CN)_2$ *Discard.*	*Treat the solution, which is now free from hydrocyanic acid, with a little caustic soda solution (free from halogen), boil and filter off the precipitate of $Ni(OH)_2$, divide the filtrate into two parts and use one part for the HBr and HI tests and the other for the HCl test.*	
	Tests for HI and HBr.	Test for HCl.
	Make the solution acid with dilute H_2SO_4, add chlorine water drop by drop, and shake the solution with CS_2 or $CHCl_3$. If the latter is colored violet, HI is present. By further addition of chlorine water, the CS_2 or $CHCl_3$ is decolorized completely if HBr is absent, but turned yellowish-brown if HBr is present. If too much chlorine water is used a wine-yellow color is produced.	*Make the solution slightly acid with HNO_3, and add dilute $AgNO_3$ drop by drop. AgI and AgBr are first precipitated (yellow). Filter and add more $AgNO_3$. If the precipitate still appears yellow, filter through a new filter, and again add $AgNO_3$ to the filtrate until a white precipitate of AgCl is formed if HCl is present.*

* If ferricyanic acid is present also add a little ferrous sulfate. Ferrocyanic acid is completely precipitated by nickel sulfate.

Group II

The members of this group are almost always detected in the preliminary examination. The special tests for these acids are described on p. 349 *et seq.*

Group III

SO_2, CO_2, $H_2C_2O_4$ are recognized in the preliminary examination. HPO_3, $H_4P_2O_7$, HBO_2, and $H_2C_4H_4O_6$ are tested for separately by the special reactions described on p. 369 *et seq.*

Group IV

CrO_3, H_3PO_4, and $H_2S_2O_3$ are detected in the preliminary examination, and in the analysis for metals.

Group V

$HClO_3$ and HNO_3 are usually detected in the preliminary examination. Their presence is, however, always confirmed by the procedure described on p. 425.

Groups VI and VII

These acids are usually detected in the preliminary examination. Their presence is confirmed by the tests described under H_2SO_4, HF, and SiO_2.

Examination for Acid Constituents (Anions)

METHOD OF A. A. NOYES.*

According to this simplified method of testing for the common acidic constituents likely to be present in minerals and commercial products, the substances are classified into (1) natural substances and igneous products and (2) non-igneous products.

The first class includes minerals, ores, slags, mattes, glasses, porcelains, abrasives and other ceramic products. These substances are examined for borate, carbonate, chloride, cyanide, fluoride, phosphate, silicate, sulfide and sulfate. The second class includes such industrial products as ordinary chemicals, pigments, fertilizers and commercial preparations which are not high temperature products. These substances are tested for arsenate, arsenite, borate, bromide, carbonate, chlorate, chloride, chromate, cyanide, ferrocyanide, ferricyanide, fluoride, hypochlorite, iodide, nitrate, nitrite, oxalate, phosphate, silicate, sulfate, sulfide, sulfite and thiocyanate.

Phosphate and silicate are detected during preparation of the solution and examination for basic constituents.

Analysis of Natural Substances and Igneous Products

TABLE XXI. — DETECTION OF SULFATE, CARBONATE, SULFIDE AND CYANIDE

Boil 0.5 g. of the substance with HCl and Zn, collecting 3 cc. of distillate in $Ba(OH)_2$ solution; filter the mixture left in the distilling flask. (1)

Filtrate: *Add $BaCl_2$.* White precipitate of $BaSO_4$ shows sulfate. (2)	Distillate: A white precipitate of $BaCO_3$ shows carbonate. The solution may contain dissolved BaS and $Ba(CN)_2$.	
	To a part of the solution add $HC_2H_3O_2$ and $Pb(C_2H_3O_2)_2$. A black precipitate of PbS shows sulfide. (3)	*To the rest of the solution add $FeCl_2$, boil and add HCl.* The formation of Prussian blue shows cyanide. (3)

PROCEDURE

1. Place 0.5 g. of the finely-powdered substance, about as much granulated zinc and 10 cc. of 3-normal HCl, which has just been boiled for a minute in a test tube, in the 50 cc. flask *A* of Fig. 26. Both of the flasks shown in the drawing are made of

* *Qualitative Chemical Analysis, 8th Edition*, 1920. This method of analysis is well suited for the use of large classes with a limited time assigned for the study of the subject.

hard glass. The safety tube *B* is about 25 cm. long and reaches nearly to the bottom of *A*. The delivery tube *C* is about 50 cm. long and extends only to the bottom of the rubber stopper in *A* but nearly to the bottom of flask *D* which rests in a beaker of cold water and contains 25 cc. of barium hydroxide solution. Both flasks are provided with two-holed rubber stoppers but one of the holes is left open in the flask *D*.

Heat the mixture in the flask *A* and slowly distill about 3 cc. of liquid into *D*. Examine the liquid that remains in *A* by § 2 and the liquid in *D* by § 3.

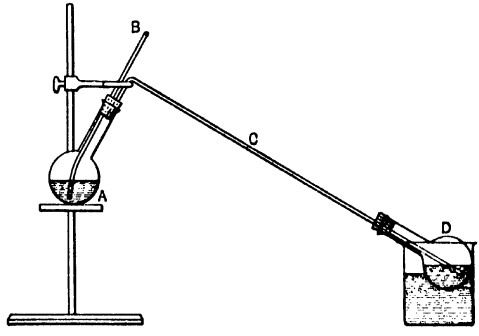

FIG. 26

2. Filter the contents of flask *A* and add barium chloride to the filtrate. *A white precipitate of barium sulfate shows the presence of sulfate.*

3. Take two-thirds of the liquid in the flask *D* and add acetic acid, 1 cc. at a time, until the solution reddens blue litmus paper. A white precipitate of $BaCO_3$ which dissolves partly or completely upon adding the acid shows that a carbonate is present. In case only a slight turbidity is obtained, compare it with the result obtained by carrying out the distillation test with acid and zinc alone.

TABLE XXII. — DETECTION OF CHLORIDE, FLUORIDE AND BORATE

Distill 1 *g. of the substance* (A) *with* H_2SO_4 *alone and* (B) *with* H_2SO_4 *and* CH_3OH. (4)

A.	B.
Test a portion of the first distillate with $AgNO_3$. A white precipitate of AgCl shows the presence of a chloride. *Test another portion with* $CaCl_2$. A white precipitate of CaF_2 shows the presence of fluoride. (5)	*Test the second distillate with HCl and turmeric solution.* An orange or red color shows borate. (6)

Add 5 cc. of lead acetate solution: *a black precipitate of PbS shows the presence of a sulfide.* In doubtful cases a blank test must be made with the acid and zinc alone, carrying out the distillation in exactly the same manner.

Test the remainder of the distillate for cyanide by adding 1 cc. of $FeCl_2$ solution, boiling for a minute and finally making acid with HCl. *The formation of Prussian blue shows the presence of a cyanide.*

4. Place 1 g. of finely-powdered substance, 3 cc. of water and 3 cc. of concentrated H_2SO_4 in the distilling flask *A* of Fig. 28 and pour 5 cc. of water into flask *D*. Distill until the liquid in *A* becomes oily in appearance and the flask is filled with white fumes. During the distillation take away the flame from under the flask for a moment, to allow the liquid in the safety-tube to run back into the flask; do this twice. Test the distillate for chloride and fluoride as described in § 5. After the solution in the distilling flask has cooled to room temperature, add to it 8 cc. of methyl alcohol and mix by shaking. Distill off most of the alcohol, catching the distillate in 8 cc. of 12-normal HCl diluted with 3 cc. of water. Examine this second distillate by § 6.

5. Boil the first distillate obtained by § 4 for about a minute and filter if it is turbid. To about one-fourth of it add 2 cc. of 6-normal HNO_3 and a little $AgNO_3$ solution. *A white precipitate of AgCl shows the presence of chloride.* To the remainder of the distillate add 5 cc. of $CaCl_2$ solution and allow the mixture to stand fifteen minutes. *A white precipitate of* CaF_2 *shows the presence of fluoride.* Confirm by the Daniel test described on page 435.

6. Transfer the second distillate of § 4 to a graduate, dilute to 20 cc. and add 2 drops of alcoholic turmeric solution (cf. p. 77). *An orange or red color shows the presence of borate* (cf. p. 381).

TABLE XXIII. — DETECTION OF SULFATE, FLUORIDE, BORATE AND SILICATE IN SUBSTANCES UNDECOMPOSED BY ACIDS

Fuse the substance with Na_2CO_3 *and extract the melt with water, rejecting the insoluble residue. Divide the solution into two portions.* (7)

Take two-thirds of the aqueous extract and evaporate to about 6 cc. Add HCl, filter, reject the precipitate and add $BaCl_2$ *to the filtrate. Filter.* (8)		*To the remainder of the aqueous extract add HCl and evaporate to dryness. Add HCl to the residue, dilute and filter.* (10)	
Precipitate: A white precipitate of $BaSO_4$ shows sulfate.	Filtrate: *Add* $NaC_2H_3O_2$ *and* $CaCl_2$. A white precipitate of CaF_2 shows fluoride. (9)	A gelatinous precipitate of H_2SiO_3 shows silicate. (11)	*Test the filtrate for borate with alcoholic turmeric solution.* A red or orange color shows borate. (12)

7. If the original substance is not decomposable by treatment with mineral acids in an open dish, or an insoluble residue is left after such treatment, the above-described tests for sulfate, fluoride and borate are likely to give negative results even when these acid constituents are present. Fuse 1 g. of the original substance, or the residue insoluble in acids, with 6 times as much anhydrous sodium carbonate in

a 30 cc. nickel crucible over a Méker burner. Protect the contents of the crucible from the combustion products of the illuminating gas by keeping the crucible covered and by placing it in a hole in a sheet of asbestos paper, fitted tightly so that the asbestos paper comes only a little below the upper edge of the crucible. After the fusion, cool the crucible and place it in 40–60 cc. of water. Boil until the fused mass is disintegrated and filter. Reject the insoluble residue or use it for tests for basic constituents.

8. Evaporate two-thirds of the aqueous extract to about 6 cc. and add 6-normal HCl, ten drops at a time, until the stirred solution is acid to litmus. Filter and reject any precipitate. Add 1 cc. of HCl to the filtrate and a little $BaCl_2$ solution. *A white precipitate of $BaSO_4$ shows the presence of sulfate.* Since illuminating gas contains a little sulfur, sometimes a slight turbidity is due to this source. In doubtful cases a blank test should be made by fusing the same quantity of sodium carbonate in the nickel crucible without any of the substance to be tested.

9. Filter off any barium sulfate obtained in § 8 and test with more $BaCl_2$ to make sure that the precipitation of sulfate was complete. Add 10 cc. of 3-normal $NaC_2H_3O_2$ solution and 10 cc. of $CaCl_2$ reagent. *A white precipitate of CaF_2 forming within 15 minutes shows the presence of fluoride.* Confirm as in § 5.

10. Make the remainder of the aqueous extract obtained in § 7 slightly acid with HCl and test for silicate as described on page 444.

11. Filter off any silicic acid obtained in § 10 and test the filtrate with 5 cc. of 12-normal HCl, 8 cc. of C_2H_5OH and 2 drops of alcoholic turmeric solution as in § 6.

Analysis of Non-Igneous Commercial Products

TABLE XXIV. — PREPARATION OF THE SOLUTION, GROUP TESTS

Boil 2.5 g. of the fine powder with 3-normal Na_2CO_3 solution, filter and wash the residue. Examine it for sulfide as in Table XXI. Use the solution for the tests outlined below and in Tables XXV–XXIX.

A	B	C	D
Add $AgNO_3$, $NaNO_2$ and HNO_3. A precipitate shows the presence of a member of the CHLORIDE GROUP. *Examine for* S^{--}, CN^-, $[Fe(CN)_6]^{--}$, $[Fe(CN)_6]^{---}$, SCN^-, Cl^-, Br^-, I^-, ClO^- *and* ClO_3^- *by* Tables XXV, XXVI and XXVII.	*Add $HC_2H_3O_2$, $BaCl_2$ and $CaCl_2$.* A precipitate shows the presence of one or more members of the SULFATE GROUP. *Test for* SO_4^{--}, SO_3^{--}, CrO_4^{--}, F^- *and* $C_2O_4^{--}$ *by Table XXVIII.*	*Add $MnCl_2$ and HCl.* A dark color of $MnCl_2$ shows the presence of an OXIDIZING ACIDIC CONSTITUENT. If it is not obtained, further tests for $[Fe(CN)_6]^{---}$, ClO^-, ClO_3^-, CrO_4^{--}, NO_3^- and NO_2^- are unnecessary.	*Add HCl, $FeCl_3$ and $K_3[Fe(CN)_6]$.* The formation of Prussian blue indicates the presence of a REDUCING ACID CONSTITUENT. If it is not obtained further tests for S^{--}, $[Fe(CN)_6]^{----}$, I^-, SO_3^{--} and NO_2^- are unnecessary.

PROCEDURE

Gently boil 2.5 g. of the finely-powdered substance with 25 cc. of 3-normal Na_2CO_3 in a covered porcelain dish. Filter and wash the residue with hot water,

and test it for sulfide only by the method outlined in Table XXI. Dilute the aqueous extract to 30 cc. and use portions of it for the tests *A*, *B* and *C* below and for further tests according to Tables XXV–XXIX.

A. To 1 cc. of the Na_2CO_3 solution, add 5 cc. of water, 3 drops of chloride-free, 3-normal $NaNO_2$ solution, 1 cc. of $AgNO_3$ reagent and 2 cc. of 6-normal HNO_3. If a precipitate of insoluble silver salt is formed, examine it according to Table XXV.

B. Dilute 2 cc. of the Na_2CO_3 solution with an equal volume of water, add 6-normal $HC_2H_3O_2$, 5 drops at a time, until the stirred solution is acid to litmus paper, and add as much more acid in excess. Filter if necessary and add 1 cc. of $BaCl_2$ reagent and 3 cc. of $CaCl_2$ reagent. Heat to boiling and allow to stand 10 minutes. If a precipitate forms of insoluble barium or calcium salt, test another portion of the $NaCO_3$ solution by the method outlined in Table XXVIII.

C. To 1 cc. of the Na_2CO_3 solution, add 4 cc. of a saturated solution of $MnCl_2$ in concentrated HCl and heat nearly to boiling. A dark brown or black color of $MnCl_3$ shows that a nitrate, nitrite, chlorate, hypochlorite, permanganate, chromate or ferricyanide is present. If the test is not obtained, these acids are absent.

D. To 1 cc. of the Na_2CO_3 solution add 3 cc. of water, 1 cc. 6-normal HCl, 2 drops of $Fe(NO_3)_2$ reagent and 2 drops of $K_3[Fe(CN)_6]$ reagent. A blue or green coloration (Prussian blue) indicates the presence of sulfide, ferricyanide, iodide, sulfite or nitrite. If it is not obtained these acid constituents are not present in the Na_2CO_3 solution.

In case a positive indication was obtained in C, test a 2-cc. portion of the Na_2CO_3 solution for nitrate and nitrite by Table XXIX. In all cases examine a 3-cc. portion of the Na_2CO_3 solution for borate according to Table XXIX. If arsenic was found present in the examination for cations, examine a 3-cc. portion of the Na_2CO_3 solution for arsenite and arsenate by Table XXIX.

TABLE XXV. — SEPARATION OF THE CHLORIDE GROUP INTO SUBGROUPS

To 6 cc. of Na_2CO_3 solution (Table XXIV) add $Pb(NO_3)_2$ and filter if necessary. (1)

Black precipitate of PbS shows sulfide.	Filtrate: *Add $HC_2H_3O_2$ and $Ni(NO_3)_2$ solution.* (2)		
	Precipitate: $Ni_2[Fe(CN)_6]$, $Ni_3[Fe(CN)_6]_2$, $Ni(CN)_2$. See Table XXVI	Filtrate: may contain SCN^-, I^-, Br^-, Cl^-, ClO_3^-. *Add $AgNO_3$ and HNO_3.* (3)	
		Precipitate: AgSCN, AgI, AgBr, AgCl. See Table XXVII.	Filtrate: may contain ClO_3^-. *Add $NaNO_2$. A white precipitate of AgCl indicates chlorate or hypochlorite.* (4)

1. If $AgNO_3$ produced a precipitate by the procedure given in Table XXIV, the color of the precipitate often shows which member of this group is present. Thus Ag_2S is black, AgI is yellow, AgBr is light yellow, $Ag_3[Fe(CN)_6]$ is orange, AgCl, Ag(CN), AgSCN, and $Ag_4[Fe(CN)_6]$ are white. The white precipitates darken,

however, on exposure to light. To test systematically for the various members of the chloride group, proceed as follows:

Add 5 cc. of water and 1 drop of normal $Pb(NO_3)_2$ solution to 6 cc. of the Na_2CO_3 solution. *If a gray or black precipitate of PbS is formed, sulfide is present.* A white precipitate of basic lead carbonate shows that sulfide is absent. Filter off the precipitate and reject it.

2. Add 6-normal $HC_2H_3O_2$ to the filtrate, 10 drops at a time, until the stirred solution is acid to litmus and then one-third as much more of the acid. Filter off any precipitate and reject it. To the solution add 3–10 cc. of normal $Ni(NO_3)_2$ solution and allow the mixture to stand 10 minutes with frequent shaking. If a precipitate of $Ni(CN)_2$, $Ni_2[Fe(CN)_6]$ or $Ni_3[Fe(CN)_6]_2$ forms, filter it off, wash it thoroughly with water and examine it according to Table XXVI. If the precipitate is so slimy that it is hard to filter, add some filter paper pulp, shake vigorously for a minute or two, and filter with gentle suction.

3. To the filtrate from § 2, add 2 cc. of 6-normal HNO_3 and some $AgNO_3$ solution. If a black precipitate forms of Ag_2S, owing to the addition of an insufficient quantity of lead salt, add 5 cc. more of HNO_3 and boil gently for a minute or two. A white precipitate indicates the presence of a chloride or thiocyanate, a yellow precipitate indicates an iodide or bromide. Filter and examine the filtrate by Table XXVII and the filtrate by the following treatment, in case an oxidizing constituent was found in Test C of Table XXIV.

4. Add a few drops more of $AgNO_3$ solution and 5 to 20 drops of chloride-free, 3-normal $NaNO_2$ solution. A white precipitate of AgCl indicates the presence of a chlorate or hypochlorite. Since hypochlorite is changed into chlorate by boiling with Na_2CO_3 it is necessary to test the original substance for chlorate and hypochlorite.

Treat 0.5 g. of the original substance with 10 cc. of cold water, shake and filter. To one-half of the filtrate add 6-normal $HC_2H_3O_2$, a few drops at a time, until the solution is acid. Then add 3 cc. of $Pb(C_2H_3O_2)_2$ reagent, heat to boiling and allow to stand 5 minutes. A brown precipitate of PbO_2 shows that hypochlorite is present (cf. p. 316). In case a positive test for hypochlorite is obtained, to the other half of the aqueous solution add 20 cc. more of water, 5 cc. of HNO_3 and 5 cc. of normal, chloride-free $NaAsO_2$ solution, and 5 cc. of $AgNO_3$ reagent. The sodium arsenite reduces the hypochlorite to chloride without affecting the chlorate. Filter off the silver chloride and reduce any chlorate in the filtrate with $NaNO_2$ solution. A white precipitate of silver chloride now shows the presence of chlorate. It is so difficult to get reagents free from chloride, that often a turbidity is obtained here when no chlorate is present. The behavior of a chlorate with concentrated sulfuric acid is characteristic and should always be used as a confirmatory test for chlorate (cf. p. 423).

5. Pour a 10-cc. portion of 3-normal NH_4OH three times through the precipitate of insoluble nickel salt obtained according to Table XXV. To the ammoniacal solution, add 2–5 cc. of $AgNO_3$ and normal Na_2SO_3 solution, a few drops at a time and shaking after each addition, until any brown color disappears. If a precipitate forms, examine it by § 6 and the remaining solution by § 7.

6. *A white precipitate of $Ag_4[Fe(CN)_6]$ shows that ferrocyanide or ferricyanide was present in the original substance.* Treat the precipitate on the filter with 1 cc. of 6-normal HCl mixed with an equal volume of normal $Fe(NO_3)_3$ solution. The formation of Prussian blue confirms the last conclusion. To determine whether ferrocyanide or ferricyanide was originally present, dilute 1 cc. of the original Na_2CO_3

solution (Table XXIV) with 5 cc. of water and add 1 cc. of 6-normal HNO_3 and 1 cc. of normal $Fe(NO_3)_3$ solution. The formation of Prussian blue shows the presence of ferrocyanide. Filter, repeatedly if necessary, and add 1 cc. of $FeCl_3$ solution. *The formation of Prussian blue now shows that a ferricyanide was present.*

TABLE XXVI. — DETECTION OF THE SEPARATE CYANIDES

Treat the nickel precipitate of Table XXV on the filter with 3-normal NH_4OH. To the solution thus obtained, which may contain $[Ni(NH_3)_4](OH)_2$, $(NH_4)_4[Fe(CN)_6]$, $(NH_4)_3[Fe(CN)_6]$, and NH_4CN, *add* $AgNO_3$ and Na_2SO_3. (5)

<table>
<tr><td rowspan="3">Precipitate: $Ag_4[Fe(CN)_6]$. Add HCl and $Fe(NO_3)_3$. A blue residue of Prussian blue (and white AgCl) shows ferrocyanide or ferricyanide. (6)</td><td colspan="3">Filtrate: $NH_4[Ag(CN)_2]$, $Ni(NO_3)_2$, $AgNO_3$ and NH_4NO_3. Add HNO_3.</td></tr>
<tr><td colspan="2">Precipitate: $Ag_2(CN)_2$, add $(NH_4)_2S$. (7)</td><td rowspan="2">Filtrate: Ni^{++}, Ag^+ and NH_4^+ as nitrates. Reject.</td></tr>
<tr><td>Residue: Ag_2S. Reject.</td><td>Solution: NH_4CNS. Add $Fe(NO_3)_3$. Red color shows cyanide. (8)</td></tr>
</table>

TABLE XXVII. — DETECTION OF THIOCYANATE, IODIDE, BROMIDE AND CHLORIDE

Silver Precipitate from Table XXV, § 3: AgSCN, AgI, AgBr, AgCl. *Treat with NH_4OH and $(NH_4)_2S$.* (9)

<table>
<tr><td rowspan="4">Residue: Ag_2S.</td><td colspan="4">Solution: may contain SCN^-, I^-, Br^- and Cl^- as ammonium salt. Add HNO_3, $Fe(NO_3)_3$ and CCl_4. Shake and allow two layers to form. (10)</td></tr>
<tr><td>CCl_4 layer: Purple color shows iodide.</td><td colspan="3">Water layer: Br^-, Cl^-, $Fe(SCN)_3$ and some I_2. Red color shows thiocyanate. Boil off iodine, cool, add $KMnO_4$ and CCl_4. (11)</td></tr>
<tr><td></td><td>Vapor: I_2.</td><td>CCl_4 layer: Br_2. Orange color shows bromide.</td><td colspan="2">Water layer: Boil off all of Br_2 add $NaNO_2$ and $AgNO_3$. (12)</td></tr>
<tr><td></td><td></td><td></td><td>Vapor: Br_2.</td><td>Precipitate: AgCl shows chloride.</td></tr>
</table>

7. To the filtrate from the insoluble $Ag_4[Fe(CN)_6]$ obtained in § 5, add HNO_3 until the odor of NH_3 disappears and then 5 cc. more of acid. *The formation of a white precipitate indicates the presence of a cyanide.* Filter and reject the filtrate.

8. Pour repeatedly through the filter a 5-cc. portion of $(NH_4)_2S$ reagent, evaporate the solution just to dryness and add to the residue 2 cc. of HCl and 2 cc. of $Fe(NO_3)_3$ solution. A red color of ferric thiocyanate confirms the cyanide test (cf. p. 333).

9. Transfer the precipitate of insoluble silver salt (Table XXV, § 3) to a small porcelain dish and digest it with 5 cc. of concentrated NH_4OH. Add $(NH_4)_2S$, 10 drops at a time, until after heating the mixture nearly to boiling and letting the precipitate settle, the reagent causes no further precipitation of silver sulfide. Filter and reject the precipitate.

10. Evaporate the filtrate until it no longer smells of ammonia, add 5 cc. of water and filter off any precipitate. Pour the solution into a small separatory funnel, add 1 cc. of 6-normal HNO_3, 3–8 cc. of normal $Fe(NO_3)_3$ solution and 1 cc. of CCl_4. Shake the mixture well and allow it to settle. *A purple color of the lower layer shows that an iodide was present* (cf. p. 324). If an iodide is absent, pass at once to § 11. *A red color of the aqueous layer* shows presence of thiocyanate or much iodide.

TABLE XXVIII. — DETECTION OF SULFATE, SULFITE, CHROMATE, FLUORIDE AND OXALATE

To 6 cc. of Na_2CO_3 solution (Table XXIV) *add $AgNO_3$ solution if sulfide was found by* § 1 *or thiocyanate by* § 10. *Acidify with HCl and filter if necessary. Add $BaCl_2$.* (13)

Precipitate: $BaSO_4$ shows sulfate.	Filtrate: may contain SO_3^{--}, $Cr_2O_7^{--}$, F^-, $C_2O_4^{--}$. *Add Br_2 solution.* (14)		
	Precipitate: $BaSO_4$ shows sulfite.	Filtrate: may contain $Cr_2O_7^{--}$, F^-, $C_2O_4^{--}$. *Add $NaC_2H_3O_2$ and $CaCl_2$.* (15)	
		Yellow precipitate: $BaCrO_4$. White precipitate: CaF, CaC_2O_4.	
		Test a part of the precipitate for fluoride by the Daniel test on page 435. (16)	*Dissolve a part of the precipitate in HNO_3, add $KMnO_4$ and distill, catching the vapors in $Ba(OH)_2$ solution.* A white precipitate of $BaCO_3$ shows oxalate. (17)

If iodide is present, draw off the CCl_4 layer, add 3 cc. of fresh CCl_4 and shake. Draw off the bottom liquid and repeat these operations until the CCl_4 no longer shows a purple color. Transfer the aqueous solution to a porcelain dish and boil for one minute. Pour back into the separatory funnel, add 1 cc. of CCl_4 and shake. *A red color of the aqueous solution shows thiocyanate.*

11. Add to the mixture in the separatory funnel, 2 cc. of 6-normal HNO_3 and then 0.2-normal $KMnO_4$, 2 drops at a time, until the aqueous layer shows the purple

color of permanganate. Shake and allow the two liquids to settle. *A yellow or orange color in the CCl_4 layer shows the presence of bromide.*

12. Transfer the aqueous solution to a flask, dilute to about 40 cc. with water. If bromide or thiocyanate has been found, boil the mixture for 5 minutes, adding more $KMnO_4$ if the mixture loses its purple color. Add 3-normal, chloride-free $NaNO_2$ solution until the mixture is decolorized and any precipitated manganese dioxide has dissolved. Then add a little $AgNO_3$. *A white precipitate of silver chloride shows the presence of chloride.*

13. If a precipitate was obtained in the procedure of Table XXIV *B*, take 6 cc. of the original Na_2CO_3 solution (Table XXIV) and, if sulfide or thiocyanate has been found present by § 1 or § 10, add an excess of $AgNO_3$ solution. If these acidic constituents are not removed some sulfate will be formed in § 14 when bromine is added. Filter and make the filtrate slightly acid by adding HCl, 10 drops at a time. Filter off and reject any precipitate of silver chloride. Add 1 cc. more of HCl and 5 cc. of $BaCl_2$ solution. *A white precipitate of $BaSO_4$ shows sulfate.*

14. Filter off any $BaSO_4$ and add saturated bromine water, 1 cc. at a time, until the liquid after shaking smells of it. Heat nearly to boiling. *A white precipitate of $BaSO_4$ shows sulfite.* Filter off the precipitate.

15. To the filtrate add 10 cc. of 3-normal $NaC_2H_3O_2$ solution and 10 cc. of normal $CaCl_2$ solution. A yellow precipitate shows chromate. A white precipitate may be fluoride or oxalate. Shake well and pour one-half of the mixture through each of two filters, rejecting the filtrates. Wash the precipitates well with water.

16. Treat one portion of the precipitate as outlined on page 435 to determine whether fluoride is present.

TABLE XXIX. — DETECTION OF NITRATE, NITRITE, BORATE, ARSENATE AND ARSENITE.

Use the sodium carbonate solution obtained according to Table XXIV for these tests.

If oxidizing acidic constituent was found according to Table XXIV, C, boil 2 cc. of the solution with NaOH and Al. Test the vapors for NH_3 with K_2HgI_4. A red precipitate of $HgO \cdot HgNH_2I$ shows nitrite or nitrate. (18)	*If a test for either nitrite or nitrate was obtained, add HC_2H_3O and CSN_2H_4.* Evolution of N_2 and formation of a red $Fe(SCN)_3$ on adding $FeCl_3$ shows nitrite. (19)	*Add HCl, C_2H_5OH and turmeric solution.* An orange color shows borate. (20)	Add HNO_3, NH_4OH and $Mg(NO_3)_2$. (21)	
			Precipitate: $MgNH_4AsO_4$. *Add $AgNO_3$ solution. A* red residue of Ag_3AsO_4 shows arsenate. (22)	Filtrate: may contain AsO_2^-. *Introduce H_2S.* A yellow precipitate of As_2S_3 shows arsenite. (23)

17. Treat the other portion of the precipitate to determine the presence of oxalate as follows: Pour a 5-cc. portion of hot, 6-normal HNO_3 several times through the filter and transfer the solution to the flask *A* of Fig. 28. Add 5 cc. of 0.2-normal

$KMnO_4$ which has been previously made acid with HNO_3 and heated to boiling. Boil the contents of the flask for 2 or 3 minutes and catch the distillate in 25 cc. of $Ba(OH_2)$ solution. A white precipitate of $BaCO_3$ shows oxalate (cf. p. 384).

18. If a positive test with $MnCl_2$ reagent was obtained, test for nitrate or nitrite to see if ammonia can be formed by reduction with aluminium in alkaline solution. If the original substance contains ammonium, boil 2 cc. of the sodium carbonate solution, obtained as outlined in Table XXIV, with 10 cc. of water and 3 cc. of 6-normal sodium hydroxide until the volume of liquid has been reduced one-third. If no ammonium salt is present in the original substance, this boiling is unnecessary unless the sodium carbonate solution has stood for some time in the laboratory. To the cold alkaline solution containing Na_2CO_3 and NaOH, add about 0.5 g. of aluminium turnings and heat gently so as to keep up a brisk evolution of hydrogen. Hold in the vapors a glass rod wet with Nessler solution. *An orange or red precipitate on the rod shows the presence of nitrate or nitrite.*

To estimate the quantity of nitrate or nitrite carry out the test so that the escaping vapors pass into a test tube containing 5 cc. of cold water, which is kept cool by placing it in a beaker of water. To the distillate add Nessler solution until no more precipitate is formed and compare the quantity of precipitate with that produced in solutions of ammonium chloride containing a known quantity of the salt.

19. If a positive test was obtained in 18, take another 1-cc. portion of the original Na_2CO_3 solution and add gradually 1 cc. of 6-normal acetic acid. (If thiocyanate or iodide has been found present, shake 1 cc. of the sodium carbonate solution with about 0.5 g. of solid Ag_2CO_3 and filter.) Add 1 cc. of 6-normal acetic acid and an equal volume of a 10 per cent solution of thiourea. Let the mixture stand 5 minutes. *The formation of gas bubbles indicates a nitrite.* Add 1 cc. of HCl and 1 cc. of $Fe(NO_3)_3$ solution. *A red color proves that nitrite is present.* If no red color is obtained, a nitrate is present. (In this scheme of analysis no provision is made for detecting a nitrate in the presence of a nitrite. Cf. p. 421.)

20. To just 3 cc. of the original sodium carbonate solution, add just 8 cc. of 12-normal HCl in small portions. Add 8 cc. of ethyl alcohol, allow the sodium chloride to settle out and decant the solution into another test tube. Add from a dropper, just two drops of turmeric dissolved in ethyl alcohol and allow the mixture to stand 10 minutes. *An orange or red color shows the presence of borate.* Compare the color with that obtained with a known quantity of sodium borate.

Chlorate, nitrate, nitrite and chromate affect the color of turmeric and when iodide is present there is sometimes trouble caused by the liberation of iodine during this test. In case any of these interfering constituents are present, evaporate 3 cc. of the sodium carbonate solution to dryness, add carefully 2 cc. of 12-normal HCl and again evaporate to dryness. To the residue add 1 cc. of 3-normal Na_2CO_3 solution and 2 cc. of water, heat to boiling and filter if necessary. Then apply the borate test as described above. During this treatment a part of the boric acid will be lost by volatilization.

21. In case arsenic was found present in the examination for cations, dilute 5 cc. of the Na_2CO_3 solution with twice as much water and add HNO_3, 1 cc. at a time, until an acid reaction is obtained. Then add 6-normal NH_4OH a few drops at a time until the stirred mixture turns red-litmus blue, avoiding an excess. Filter if necessary and add 10 cc. of $Mg(NO_3)_2$ reagent. Let the mixture stand 10 minutes with frequent shaking. Filter and wash any precipitate with normal NH_4OH. *A white precipitate of $MgNH_4AsO_4$ shows the presence of arsenate or phosphate.* Test the filtrate with hydrogen sulfide to see if it contains any arsenic in the trivalent

condition. An immediate precipitation of yellow As_2S_3 shows the presence of arsenite.

Pour on to the filter containing the insoluble magnesium salt a 1-cc. portion of $AgNO_3$ solution to which a few drops of acetic acid have been added. A dark red residue shows the presence of arsenate. In case the residue is yellow and there is doubt whether any arsenate is present, pour a 5-cc. portion of 6-normal HCl through the filter a number of times and add 1 cc. of KI solution and 1 cc. of CCl_4. Shake and if the carbon tetrachloride becomes purple, an arsenate is present. (Cf. p. 246.)

In case a precipitate of doubtful color was obtained in the As_2S_3 test, examine the precipitate for arsenic as outlined in Table XI, p. 292.

Detection of Carbonate and Sulfide in the Original Substance. Test as described under Table XX, § 3.

B. THE SUBSTANCE IS A METAL OR AN ALLOY

The analysis of a metallic alloy is much simpler than that of a mixture of salts, because there are no acids to test for. Of the electro-negative elements, usually only phosphorus, silicon, carbon, and sulfur have to be considered.

As all common metals, with the exception of gold, platinum, tin, and antimony, are soluble in nitric acid, alloys are usually brought into solution by dissolving therein, and the use of aqua regia is only necessary in a few cases. Many alloys rich in silicon (e.g., copper silicide) are extremely difficultly soluble even in aqua regia, and are best brought into solution by fusing with caustic alkali in a silver crucible, and afterwards dissolving the melt in nitric acid.

It is not advisable to dissolve an alloy in hydrochloric acid, for phosphides, carbides, silicides, sulfides, and arsenides, which are often present in small amounts, are decomposed by this acid in such a way that the negative elements are evolved as hydrogen compounds, and thus escape detection. For the analysis of ordinary alloys, the following procedure is used:

Place 1 or 2 gms. of the alloy (best in the form of borings) in a 200-cc. porcelain dish and treat them under a good hood with about 20 cc. of nitric acid, sp. gr. 1.25–1.30 (1 vol. conc. HNO_3 + 1 vol. H_2O). After the first violent reaction is over, carefully evaporate (with constant stirring) almost to dryness, being careful to avoid overheating; * add a little water and heat.

(*a*) The mass dissolves completely. The alloy contains neither tin nor antimony; analyze it according to Table XXX.

(*b*) The mass does not dissolve completely, but a white, greenish residue remains; analyze according to Table XXXI.

C. THE SUBSTANCE IS A LIQUID

The color, odor, and reaction towards litmus enable one to draw important conclusions.

(*a*) The solution reacts neutral; it contains no free acid, free base, acid salt, no salt which shows an acid or alkaline reaction on account of hydrolysis, nor any insoluble salt.

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* Otherwise insoluble basic salts are likely to be formed. If this be the case, as is often shown by the dark color of the residue, add a little conc. HNO_3, heat the liquid somewhat and then dilute with water.

First of all, determine whether there are any solid substances dissolved in the liquid by evaporating a small portion to dryness at as low a temperature as possible (so as not to lose any volatile substances). If a residue remains, examine it according to A, p. 450.

(*b*) The solution reacts alkaline. An alkaline reaction may be due to the presence of hydroxides of the alkalies or alkaline earths, peroxides, carbonates, borates, cyanides, silicates, sulfides (zincates, aluminates, molybdates, tungstates) of the alkalies, as well as by ammonia or hypochlorites, etc.

If the solution, for example, contains hydroxides or carbonates of the alkalies, it is evident that substances which are precipitated by them cannot be present at the same time, except, in some cases, in the form of complex ions (cyanides, tartrates, etc.)

At once test the solution for peroxides, hydroxides, and carbonates, as well as for the sulfides of the alkalies.

To test for peroxides * (H_2O_2) heat a little of the solution with a few drops of cobalt nitrate solution; a black precipitate shows the presence of H_2O_2.† Or test the solution by adding some titanium sulfate solution and acidifying carefully with cold dilute sulfuric acid; a yellow coloration shows the presence of H_2O_2.‡

A still more sensitive reagent, according to Schöne,§ is a very dilute solution of $FeCl_3 + K_3[Fe(CN)_6]$. If the slightest trace of H_2O_2 is present in the solution, the red solution becomes greenish, and after a time Prussian blue separates out.

In order to detect the presence of hydroxides and carbonates in the presence of H_2O_2, boil a portion of the solution for a long time in a porcelain dish in order to destroy the peroxide, and then add barium chloride until no more precipitate is formed. If the solution now shows an alkaline reaction, the presence of hydroxides ‖ is assured. If the precipitate produced by barium chloride dissolves in acid with effervescence, and the gas evolved renders barium hydroxide solution turbid, carbonates are present. If the solution smells of ammonia, evaporate a small portion to dryness in order to see whether other compounds are present, and examine the residue according to A, p. 450.

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* See p. 455.

† If the alkaline solution contains hypochlorites or sulfides, these will also give a black precipitate with cobalt nitrate; the above reaction serves only to detect H_2O_2 in the absence of hypochlorites or sulfides. If these last substances are present, H_2O_2 is absent, because hypochlorites are reduced to chlorides and sulfides oxidized to sulfates by H_2O_2.

The presence of hypochlorites is usually detected by the odor; on acidifying with dilute H_2SO_4, the odor of chlorine can be detected. Sulfides give off H_2S on being acidified. Hypochlorites and sulfides cannot exist together in the same solution.

‡ H_2O_2 can also be detected by the chromic acid reaction, but this test is less certain than that with titanium sulfate.

§ Ber., **7**, 1695.

‖ Either as such in the original solution or by hydrolysis of peroxides. This test for OH^- ions in the presence of carbonates has been used for years by the author. It is reliable, though care must be taken to add an excess of $BaCl_2$, as otherwise an alkaline reaction may be due to $BaCO_3$, which is more soluble in water than in $BaCl_2$ solution.

(*c*) The solution reacts acid; it can then contain substances which are soluble in water and in acids, as well as free acids. Evaporate a small portion to dryness in order to see whether any non-volatile matter is present. If no residue is obtained, neutralize the solution with soda and test for acids. If a residue is obtained, examine it according to A, p. 450.

D. *The substance to be analyzed is a gas.*

This case is discussed in Volume II under Gas Analysis.

TABLE XXX

A. The alloy after being evaporated with nitric acid dissolves in water, forming a clear solution. The alloy contains neither *tin* nor *antimony*. *Add 2 cc. of concentrated H_2SO_4 and evaporate until white fumes of sulfuric acid come off thickly.*

RESIDUE. — **SOLUTION.**

White $PbSO_4$.

Wash the precipitate with water and confirm the presence of lead by dissolving in hot NH_4Ac solution and adding K_2CrO_4.

Can contain Bi, Cu, Cd, Fe, Mn, Ni, Co, Zn, Al, P_2O_5.
Saturate with H_2S and filter.

PRECIPITATE. — **SOLUTION.**

Bi_2S_3, CdS, CuS.
Dissolve in hot, dilute HNO_3, filter off the deposited sulfur, add an excess of NH_3 and filter.

PRECIPITATE. — **SOLUTION.**

$Bi(OH)_3$, white. *Dissolve in a little HCl and treat with an alkaline solution of $SnCl_2$.* A black precipitate shows *Bi* to be present.

$[Cu(NH_3)_4]SO_4$
$[Cd(NH_3)_6]SO_4$.
A blue-colored solution shows *Cu. Decolorize the solution by the addition of KCN, and add $(NH_4)_2S$.* A yellow precipitate of CdS shows the presence of *Cd.*

$FeSO_4$, $MnSO_4$, $NiSO_4$, $CoSO_4$, $ZnSO_4$, $Al_2(SO_4)_3$, H_3PO_4.
Expel the excess of H_2S by boiling, add a few drops of concentrated HNO_3 to oxidize the iron, then 10 cc. of NH_4Cl solution, and NH_4OH drop by drop until the boiling liquid smells of NH_3 permanently; filter the solution quickly.

PRECIPITATE. — **SOLUTION.**

$[Fe(OH)_3$, $Al(OH)_3$, $(AlFe)PO_4]$.
Dissolve in a little HNO_3, and test a little of the solution for Fe by the addition $K_4Fe(CN)_6$. The formation of Prussian blue shows presence of *Fe.*
Test another portion of the solution with considerable ammonium molybdate solution. A yellow crystalline precipitate shows the presence of *P.*
Treat the principal part of the solution with an excess of KOH and filter. Make the filtrate, which may contain any Al as $KAlO_2$, acid with HCl, and treat with NH_4OH. A white, gelatinous precipitate shows the presence of *Al.*

SOLUTION.

$MnCl_2$, $[Co(NH_3)_6]Cl_3$,
$[Ni(NH_3)_6]Cl_3$, $[Zn(NH_3)_6]Cl_2$.
Saturate with H_2S and filter. Reject the filtrate. Treat the precipitate, consisting of sulfides of Mn, Co, Ni, and Zn, with cold dilute HCl and filter.*

RESIDUE. — **SOLUTION.**

NiS, CoS. *Examine according to Table VII, p. 199.*

$MnCl_2$, $ZnCl_2$.
Boil off the H_2S, treat the solution with an excess of KOH and filter.

RESIDUE. — **SOLUTION.**

$Mn(OH)_2$. *Fuse a small portion with sodium carbonate and potassium nitrate on platinum foil.* A green melt shows the presence of *Mn.*

K_2ZnO_2. *Add acetic acid and conduct H_2S into the solution.* A white precipitate of ZnS shows *Zn* to be present.

* If neither iron nor aluminium were present in the alloy, test this filtrate for phosphoric acid. Evaporate to a small volume, filter from deposited sulfur if necessary, and test with ammonium molybdate. If the alloy contains magnesium it will be present in this filtrate and must be tested for according to p. 99, § 4.

TABLE XXXI

B. The alloy, after being evaporated with nitric acid, does not all dissolve in water. The alloy contains tin or antimony, or both.* *Filter.*

RESIDUE.	SOLUTION.
SnO_2, Sb_2O_3, (Sb_2O_5). P_2O_5, Bi_2O_3, and traces of Cu, Pb, Fe, etc. *Wash with water, add KOH to alkaline reaction, and then 5 to 10 cc. of K_2S solution. Heat for some time on the water-bath and filter. [In many cases it is more advantageous to accomplish a similar reaction by fusing with Na_2CO_3, and S in a covered porcelain crucible* (cf. p. 277).]	*Examined according to Table XXX.*

RESIDUE.	SOLUTION.
Bi_2S_3, PbS, CuS, etc. *Dissolve in HNO_3, filter off sulfur, and add the filtrate to the original solution of the alloy in nitric acid.*	K_2SnS_3, K_3SbS_3, K_3PO_4. *Dilute with water, acidify with dilute HCl, and filter.*

PRECIPITATE.	SOLUTION.
SnS_2, Sb_2S_3, or Sb_2S_5. *Dissolve in concentrated HCl, boil, dilute with a little water, filter off sulfur, and test according to Table XI, p. 292 or Table XIV, p. 296 for Sn and Sb.*	KH_2PO_4, KCl. *Evaporate the solution to a small volume, add an excess of NH_4OH and treat with magnesia mixture. A white crystalline precipitate shows H_3PO_4 or P to be present.*†

* In the case of many alloys containing silicon (iron and steel), silicic acid separates out on the addition of HNO_3. This is usually present in a very small amount, and is detected as described under silicic acid.

† This is confirmed by dissolving the precipitate in HNO_3 and testing with ammonium molybdate solution.

PART V. — REACTIONS OF SOME OF THE RARER METALS

In the treatment of the rare metals, the same method and order will be used as with common metals.

THE ALKALI GROUP

CESIUM, RUBIDIUM, LITHIUM

CESIUM, Cs. At. Wt. 132.81. M. Pt. = 26°

Occurrence. — Cesium and rubidium are not rare elements, strictly speaking, for they are found almost everywhere, but always only in very small amounts. Thus cesium replaces potassium in many feldspars and micas, and is found in many rocks which carry these minerals, as well as in mineral waters which ooze from them. Cesium and rubidium were discovered in the mother liquor of Durkheimer brine in the year 1860 by Bunsen and Kirchhoff by means of the spectroscope.

Pollucite, a mineral closely related to leucite, found at Elba and crystallizing in the regular system, is a typical cesium mineral. Its composition is $H_2Cs_4Al_4(SiO_3)_9$.

Cesium and rubidium in all their reactions behave almost exactly like potassium. The principal difference between these three metals lies in the different solubilities of their corresponding salts, as will be seen by the table given on p. 501. The metals themselves are silver white and resemble potassium. The salts also color the flame violet.

Reactions in the Wet Way

A solution of cesium chloride should be used.

1. **$H_2[PtCl_6]$** produces a yellow, crystalline precipitate which is of a lighter color than the corresponding potassium salt and is much less soluble; 100 parts of water dissolve at 0° C. only 0.024 part, and at 100° C. 0.377 part of the salt.

2. **Tartaric Acid** produces, as with potassium and rubidium, a white, crystalline precipitate, $CsHC_4H_4O_6$; 100 parts of water dissolve at 25° C. 9.7 parts, and at 100° 97.1 parts of the salt.

3. **$H_2[SnCl_6]$** (a solution of $SnCl_4$ in concentrated HCl) produces in concentrated solutions a white, crystalline precipitate of cesium

chlorostannate, $Cs_2[SnCl_6]$ (octahedrons). Ammonium salts give the same reaction, but potassium and rubidium salts do not.

4. H_3SbCl_6, a solution of antimony trichloride in concentrated hydrochloric acid, precipitates white cesium chlorantimonite.

$$3\,Cs^+ + SbCl_6^{---} \rightarrow Cs_3[SbCl_6].$$

5. $Bi(NO_3)_2$ and $NaNO_2$ precipitate a yellow double nitrite,

$$5\,Bi^{+++} + 9\,Cs^+ + 6\,Na^+ + 30\,NO_2^- \rightarrow 5\,Bi(NO_2)_3 \cdot 9\,CsNO_2 \cdot 6\,NaNO_2.$$

Reactions in the Dry Way

Cesium compounds color the flame reddish violet, very similar to the potassium flame.

Flame Spectrum. — An intensely blue double line, **455.5**$\mu\mu$, **459.3**$\mu\mu$. At higher temperatures a number of paler lines appear of subordinate importance; in the red 697.3$\mu\mu$ and 672.3$\mu\mu$, in the orange yellow 621.3$\mu\mu$ and 601$\mu\mu$, in the yellow 584.5$\mu\mu$, in the green 566.4$\mu\mu$, 563.5$\mu\mu$, 550.3$\mu\mu$, 547.1$\mu\mu$, 541.9$\mu\mu$, and 535.1$\mu\mu$. Moreover, a faint continuous spectrum is seen from the yellow to the blue. See chart.

RUBIDIUM, Rb. At. Wt. 85.45. M. Pt. = 38°

Occurrence. — Rubidium almost always accompanies cesium and is found in many mineral waters; in carnallite from Stassfurt; in lepidolite, $(Li,K,Na)_2Al_2(F,OH)_2Si_3O_9$; in triphylite, $(FeMn)(LiCsRb)PO_4$; and in spodumene, $(LiNa)Al(SiO_3)_2$ a mineral of the pyroxene group. Lepidolite from Rozena contains about 0.54 per cent Rb and 0.0014 per cent Cs. As far as the author knows, there is no typical rubidium mineral. Rubidium salt has been found in beet-root molasses.

Reactions in the Wet Way

1. $H_2[PtCl_6]$ produces, as with cesium and potassium salts, a white, crystalline precipitate of $Rb_2[PtCl_6]$, which is more difficultly soluble than the corresponding potassium salt, but more soluble than the cesium salt; 100 parts of water dissolve at 0° C. 0.134 part, and at 100° 0.634 part of the salt.

2. $H_2[SnCl_6]$ produces a white precipitate only in very concentrated solutions. The salt is much more soluble than the corresponding cesium salt, but this reaction is not suitable for separating the two metals.*

* STOLBA, *Z. anal. Chem.*, **12**, 440, recommends this reaction for separating rubidium and cesium but GODEFFROY, *Ber.*, **7**, 375, and COSSA, *Z. anal. Chem.*, **17**, 350, obtained better results with the chlorantimonite reaction.

3. **Tartaric Acid** produces a precipitate of $RbHC_4H_4O_6$ only in concentrated solutions; 100 parts of water dissolve at 25° C. 1.18 parts, and at 100° C. 94.1 parts of the salt. The corresponding cesium salt is more soluble, while that of potassium is less soluble.

4. $Bi(NO_3)_2$ and $NaNO_2$ precipitate a yellow double salt.

$$Bi^{+++} + 2\,Rb^+ + 6\,NO_2^- + Na^+ \rightarrow Bi(NO_2)_3 \cdot 2\,RbNO_2 \cdot NaNO_2.$$

Reactions in the Dry Way

Flame Coloration. — Similar to cesium.

Flame Spectrum. — Violet double lines **420.2**$\mu\mu$ and **421.5**$\mu\mu$, also the red double line 781.1$\mu\mu$ and 795.0$\mu\mu$. At higher temperatures a continuous spectrum is visible from the yellow to the blue in which the following lines are to be found in addition to those given above; in the orange-yellow 629.8$\mu\mu$, 626.1$\mu\mu$, 620.6$\mu\mu$, 617.7$\mu\mu$; in the yellow-green 572.4$\mu\mu$, 570.0$\mu\mu$, 564.8$\mu\mu$, and of subordinate importance the green lines 543.5$\mu\mu$, 536.5$\mu\mu$, and 516.8$\mu\mu$.

Separation of Potassium and Rubidium from Cesium
Method of Stolba

To the concentrated solution of alkali salts, add a solution of antimony trichloride in concentrated hydrochloric acid which causes the prompt precipitation of cesium chlorantimonite. Filter and wash with strong hydrochloric acid, using a hardened filter paper.

LITHIUM, Li. At. Wt. 6.94. M. Pt. = 186°

Occurrence. — Lithium is found to a greater extent in nature than cesium and rubidium; in triphylite, (Fe,Mn)(Li,Cs,Rb)PO_4; in petalite, Al(Li,Na,H)Si_4O_{10}, a mineral of the feldspar group (also called castorite); in amblygonite, Li(AlF)PO_4, monoclinic; in lepidolite, $Al_2(Li,K,Na)_2(F,OH)_2Si_3O_9$; in many varieties of tourmaline, and muscovite, in epidote and orthoclase, and consequently in many mineral-spring waters. In some cases as much as 36 mgs. Li are contained in a liter of spring water.

Lithium is the lightest of all metals, and floats on petroleum. It oxidizes quickly in the air, and decomposes water at ordinary temperatures, forming LiOH, which dissolves slowly in the water; the solution reacts alkaline and absorbs carbon dioxide from the air with avidity, forming difficultly soluble Li_2CO_3.

Lithium chloride is soluble, even in the anhydrous state, in a mixture of alcohol and ether as well as in amyl alcohol (difference from the remaining metals of this group).

Reactions in the Wet Way

A solution of lithium chloride should be used.

1. $H_2[PtCl_6]$ produces no precipitation.

2. **Tartaric Acid** produces no precipitation.

3. Na_2HPO_4 produces from boiling, moderately-concentrated solutions a white precipitate of tertiary lithium phosphate. The precipitation is only quantitative when the solution is made alkaline with caustic soda, evaporated to dryness, and taken up in water containing ammonia:

$$HPO_4^{--} + 3\,Li^+ + OH^- \rightarrow Li_3PO_4 + H_2O.$$

Lithium phosphate is fusible (difference from magnesium and the alkaline earths).

4. $(NH_4)_2CO_3$. If ammonium carbonate and ammonia are added to a concentrated lithium solution, lithium carbonate is precipitated in the form of a white powder. The salt, contrary to the other alkali carbonates, is very difficultly soluble in water: 100 parts of water dissolve at 13° C. 1.31 parts of Li_2CO_3. In the presence of considerable alkali chloride or of ammonium chloride, no precipitation takes place.

5. **Ammonium Fluoride** in ammoniacal solution slowly precipitates white, gelatinous lithium fluoride:

$$2\,Li^+ + F_2^{--} \rightarrow Li_2F_2.$$

One gram of the precipitate requires 3500 cc. of water to dissolve it; the same quantity of sodium fluoride requires only 70 cc. of water and the other alkali fluorides are more soluble. Carnot,* therefore, uses the reaction for the separation of lithium from the other alkalies. The reagent should be pure and free from ammonium fluosilicate.

To test for small quantities of lithium ions, evaporate the solution with hydrofluoric acid on the water bath in a platinum dish and treat the residue with a little dilute ammonia.

Reactions in the Dry Way

Flame Coloration. — Pure lithium salts impart a magnificent, carmine-red coloration to the gas-flame. If considerable amounts of sodium salts are present, the lithium flame is completely masked; but if the flame is observed through cobalt glass the red color becomes distinctly visible.

Flame Spectrum. — An intensely red line **670.3**$\mu\mu$ and at higher temperatures the pale orange-yellow line 610.3$\mu\mu$.

* *Z. anal. Chem.*, **29**, 332.

SUMMARY OF THE ALKALI METALS

	Lithium.	Sodium.	Potassium.	Rubidium.	Cesium.
Atomic Weight	6.94	23.00	39.10	85.45	132.81
Melting-point	180°	95.6°	62.5°	38.5°	26–27°
$X_2[PtCl_6]$:					
Solubility in alcohol	soluble	soluble	insoluble	insoluble	insoluble
100 parts of water dissolve at 20°	considerable	considerable	1.12	0.141	0.079
at 100°	considerable	considerable	5.13	0.634	0.377
$XHC_4H_4O_6$:					
100 parts water dissolve at 10°	considerable	considerable	0.425	—	—
at 25°	—	—	—	1.18	9.7
Alums:					
100 parts water dissolve at 17°	—	—	13.5	2.27	0.619
Chlorides:					
Solubility in alcohol-ether	soluble	insoluble	insoluble	insoluble	insoluble
Carbonates:					
Solubility in absolute alcohol	insoluble	insoluble	insoluble	insoluble	soluble

DETECTION OF LITHIUM, RUBIDIUM, AND CESIUM

In the Presence of Considerable Sodium and Potassium

Evaporate the solution containing the metals as chlorides almost to dryness, triturate the residue with 90 per cent alcohol and filter. The alcoholic solution contains all of the Li, Rb, and Cs, with small amounts of K and Na. Evaporate again nearly to dryness and once more extract with alcohol and filter. If only traces of the rare alkalies are present, the residue must be extracted several times with alcohol.

Evaporate the alcoholic extract to dryness and treat the residue with concentrated hydrochloric acid. This is done in order to change LiOH into LiCl. Some of the former is formed by evaporating the solution, and it is insoluble in alcohol-ether. Evaporate once more, gently ignite the residue over the free flame, and, after cooling, triturate the residue with ether-alcohol mixture, using a glass rod, and filter through a filter that is wet with the ether-alcohol mixture. The filtrate contains the lithium. Evaporate it to dryness and test for lithium by means of the flame reaction or in the spectroscope.

Dissolve the residue insoluble in alcohol-ether in a little water, treat with chloroplatinic acid and filter. Extract the precipitate repeatedly with small portions of boiling water, decanting off the liquid each time through the filter.

The potassium chloroplatinate dissolves in the hot water, forming a yellow solution. Continue the treatment with hot water until the residue is of a light-yellow color. Dry, place in a porcelain boat, and heat in a glass tube, made of difficultly fusible glass, in a stream of dry hydrogen; in this way the alkali chloroplatinates are reduced to chloride and platinum:

$$X_2[PtCl_6] + 2\,H_2 = 4\,HCl\uparrow + 2\,XCl + Pt.$$

After cooling, treat the residue with a little water, filter off the platinum, evaporate the solution to dryness and test in the spectroscope for Cs and Rb.

In order to detect lithium, cesium, and rubidium in a silicate undecomposable by acids (lepidolite, for example) decompose the finely powdered mineral with hydrofluoric and sulfuric acids as described on p. 446, change the sulfates to chlorides by the addition of barium chloride, and free the solution from other metals by treatment with barium hydroxide as described on p. 102, § 3, and then carry out the above separation.

ALKALINE EARTH METAL

Radium, Ra. At. Wt. 226.0

Radium, in its reactions, is very much like barium. Inasmuch as its importance is due to its physical properties and physical methods serve to detect very small quantities, the identification of this element is the work of the physicist rather than the chemist.

METALS OF THE $(NH_4)_2S$ GROUP

BERYLLIUM, ZIRCONIUM, THORIUM, YTTRIUM, ERBIUM, CERIUM, LANTHANUM, DIDYMIUM, TANTALUM, NIOBIUM

BERYLLIUM, Be, OR GLUCINUM, Gl. At. Wt. 9.1. Sp. Gr. 1.85. M. Pt. = < 1000°

Occurrence. — Chrysoberyl, $Be(AlO_2)_2$; phenacite, Be_2SiO_4; beryl, $Be_3Al_2Si_6O_{18}$; euclase, $AlBeHSiO_5$; meliphanite, $Be_2Ca_2NaSi_3O_{10}F$; and leucophanite, $BeCaNaSi_2O_6F$.

Beryllium is a bivalent metal, and forms a white oxide, BeO, which is soluble in acids. The metal is stable in the atmosphere, does not decompose water but dissolves in dilute hydrochloric and sulfuric acids and in sodium or potassium hydroxide with evolution of hydrogen

$$Be + 2\,H^+ \rightarrow Be^{++} + H_2\uparrow, \quad 2\,Be + 4\,OH^- \rightarrow 2\,BeO_2^{--} + 2\,H_2\uparrow.$$

Beryllium, like aluminium, is easily made passive by nitric acid.

Beryllium hydroxide, $Be(OH)_2$, dissolves in acids or in alkalies but after standing some time is very hard to dissolve. Beryllium closely resembles aluminium in its chemical behavior. Beryllium salts react acid in aqueous solution and possess a sweetish, astringent taste. The element is often called Glucinum, Gl, in England and the United States.

Reactions in the Wet Way

Use a solution of $BeSO_4 \cdot 4\,H_2O$.

1. **Ammonia** and **Ammonium Sulfide** produce a white precipitate of $Be(OH)_2$, similar in appearance to $Al(OH)_3$, insoluble in an excess of the precipitant, but readily soluble in HCl, forming a colorless solution. The yellow color often obtained in dissolving the hydroxide in hydrochloric acid is due to traces of ferric chloride.

2. **KOH** precipitates white, gelatinous beryllium hydroxide, readily soluble in an excess of the reagent, forming potassium beryllate:

$$Be^{++} + 2\,OH^- \rightarrow Be(OH)_2; \quad Be(OH)_2 + 2\,OH^- \rightarrow [BeO_2]^{--} + 2\,H_2O.$$

The alkali beryllates are decomposed hydrolytically on boiling their dilute aqueous solutions, all of the beryllium being precipitated as hydroxide. The precipitate thus obtained is denser than that thrown down by ammonia, and differs from the latter by being insoluble in potassium carbonate and difficultly soluble in ammonium carbonate solutions; it is also much more difficultly soluble in dilute acids. A solution containing a considerable excess of alkali hydroxide does not give a precipitate of beryllium hydroxide by boiling.

Tartaric acid prevents the precipitation of beryllium hydroxide.

3. **Ammonium Carbonate** produces a white precipitate of beryllium carbonate, readily soluble in an excess of the reagent (difference from aluminium); by boiling the solution, the beryllium is precipitated as white basic carbonate. This property is used in separating beryllium from iron and aluminium. The separation is not sharp, however, which can also be said of the separation by means of caustic potash.

According to Fresenius, it is necessary to heat the solution somewhat. In order to make a quantitative separation, the beryllium hydroxide or carbonate must be redissolved and the precipitation repeated several times.

According to Parson and Barnes * a good method for separating beryllium from aluminium consists in boiling in 10 per cent sodium bicarbonate solution; aluminium hydroxide is precipitated and beryllium remains in solution.

4. **Alkali Carbonates** give white precipitates of variable composition; usually a basic carbonate is formed. When freshly precipitated the carbonate dissolves in a large excess of sodium or potassium carbonate but is much more soluble in ammonium carbonate. By boiling the ammonium carbonate solution, reprecipitation takes place, but not by boiling the sodium or potassium carbonate solution unless it is very dilute.

5. **$BaCO_3$** precipitates beryllium as hydroxide.

6. **Oxalic Acid** and **Ammonium Oxalate** cause no precipitation (difference from thorium, zirconium, erbium, yttrium, cerium, lanthanum, and didymium).

7. **K_2SO_4** gives with beryllium sulfate a beautifully crystalline double salt, $K_2Be(SO_4)_2 \cdot 2\,H_2O$, which is soluble in a concentrated solution of K_2SO_4 (difference from Ce, La, and Di).

8. **Ether and HCl.** — $BeCl_2$ is soluble in a mixture of equal volumes of saturated aqueous and ethereal hydrochloric acid, while the hydrous aluminium chloride is not (good method for separating Be and Al).†

9. **Diammonium Phosphate** gives a gelatinous precipitate of phosphate which dissolves in a considerable excess of the reagent. By carefully adding ammonia, but avoiding an excess, a crystalline precipitate of beryllium ammonium phosphate forms on boiling. Citric acid does not prevent the precipitation, as it does with aluminium, but if considerable aluminium is present, it tends to keep the beryllium in solution.

10. **Morin** gives no fluorescence with beryllium salt solutions.

11. **Sodium Thiosulfate** gives no precipitate.

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* *Z. anal. Chem.*, **46**, 292.

† F. S. Havens, *Z. anorg. Chem.*, **18**, 147 (1898).

12. Chloroform. — To separate beryllium from aluminium ions, Haber and van Oordt * take advantage of the fact that beryllium acetate is soluble in chloroform. The hydroxides of these three elements, when freshly precipitated, are dissolved in glacial acetic acid, evaporated with a little water and the residue extracted with chloroform.

To detect small quantities of beryllium in the presence of considerable aluminium, Rössler † proceeds as follows:

Dissolve the hydroxides in hydrochloric acid, evaporate to dryness and dissolve the residue in a little water, adding a little hydrochloric acid if necessary. Rinse the solution into a heavy glass tube sealed at one end, add about twelve times as much potassium sulfate as there was aluminium and enough water to dissolve the salt on warming. Seal the tube and heat at 180° for half an hour. After cooling, open the tube, filter off the basic potassium-aluminium sulfate and precipitate the beryllium with ammonium hydroxide. To purify the beryllium hydroxide, dissolve it promptly in hydrochloric acid, add a little citric acid and throw down the beryllium as beryllium ammonium phosphate from the boiling solution.

Reactions in the Dry Way

Beryllium salts moistened with cobalt nitrate solution and heated, give a gray mass. Fused with twice as much potassium acid fluoride, HKF_2, the mass dissolves in water containing hydrofluoric acid; under the same conditions, potassium aluminium fluoride remains insoluble.

ZIRCONIUM, Zr. At. Wt. 90.6. M. Pt. < Si

Occurrence. — Zircon, $ZrSiO_4$, tetragonal, isomorphous with rutile, Ti_2O_4; thorite (orangite), $ThSiO_4$; cassiterite; Sn_2O_4; polianite, Mn_2O_4, and plattnerite, Pb_2O_4; baddeleyite, ZrO_2, monoclinic.

The metal itself is hard to obtain pure. It is usually obtained as a black, amorphous powder but it can be crystallized in the form of hard, brittle, steel-gray scales with metallic lustre. In the amorphous condition it burns below a red heat but a white heat is necessary for the crystalline condition. It is only attacked slightly by acids except aqua regia, hydrofluoric acid, and concentrated sulfuric acid; in the last case water-soluble zirconium sulfate, $Zr(SO_4)_2$, is formed.

Zirconium forms two oxides: Zirconium dioxide, ZrO_2, and zirconium pentoxide, Zr_2O_5. The former is the more important and can be dissolved by heating for a long time with a mixture of two parts of concentrated H_2SO_4 and one part of water and afterwards diluting.

The mineral zircon, $ZrSiO_4$, cannot be decomposed by such treatment. It must be finely pulverized and fused with four times as much sodium carbonate at a high

* *Z. anal. Chem.*, **40**, 465.

† *Z. anorg. Chem.*, **13**, 435.

heat in a platinum crucible; sodium silicate, Na_4SiO_4, and sodium zirconate, Na_4ZrO_4, are formed. On treating the melt with water, the former salt dissolves, while the latter is decomposed hydrolytically, forming sodium hydroxide and sandy, insoluble zirconium hydroxide; the latter retains some of the caustic soda very persistently. After washing the residue, heat it, without previous drying, with concentrated sulfuric acid at a temperature near the boiling-point; in this way anhydrous $Zr(SO_4)_2$ is obtained. By pouring water over the latter, the salt $Zr(SO_4)_2 \cdot 4\,H_2O$ is formed, which dissolves slowly in cold water, but more readily in hot water, forming a solution with an acid reaction.

The amphoteric character and tendency to form complex salts is a characteristic of quadrivalent zirconium.

Zircon is also attacked by fusing with potassium acid fluoride; potassium fluosilicate, K_2SiF_6, and potassium fluozirconate, K_2ZrF_6, are formed. Heating with carbon, to form zirconium carbide, and then heating in a stream of chlorine, or by heating with carbon tetrachloride at 450°, results in the sublimation of water-soluble zirconium chloride, $ZrCl_4$, which gives the basic chloride, $ZrOCl_2$ on treatment with a little water; the latter is soluble in water but, unlike ferric chloride, is insoluble in ether.

Reactions in the Wet Way

A solution of zirconium nitrate, $Zr(NO_3)_4$, or a freshly-prepared one of basic zirconium chloride, $ZrOCl_2 \cdot 8\,H_2O$, may be used for the following reactions:

1. **NH_4OH** and **$(NH_4)_2S$** produce a white, gelatinous precipitate of $Zr(OH)_4$, insoluble in an excess of reagent.

2. **KOH** and **NaOH** likewise produce the same precipitate insoluble in an excess of reagent (difference from Al and Be). When the zirconium hydroxide is produced in the cold it is readily soluble in dilute acids; but when thrown down from a boiling solution it is very difficultly soluble in dilute acids, though it will dissolve even then in concentrated acids without difficulty.

Tartaric acid prevents all of the above precipitations owing to the formation of the complex acid, $H_2[ZrO(C_4H_4O_6)_2]$, which gives soluble alkali salts. If ferric ions are present in the original solution, they can be precipitated by ammonium sulfide as ferric sulfide, and the zirconium, like aluminium and beryllium, remains dissolved.

3. **$(NH_4)_2CO_3$** produces a white, flocculent precipitate of basic carbonate, readily soluble in an excess of the reagent, but reprecipitated by boiling.

4. **K_2CO_3** and **Na_2CO_3** produce white precipitates somewhat soluble in an excess, but reprecipitated by ammonia.

5. **$BaCO_3$** causes incomplete precipitation, even on boiling.

6. **Oxalic Acid** gives a white, flocculent precipitate of zirconium oxalate, readily soluble in an excess of oxalic acid, difficultly soluble in dilute hydrochloric acid, and readily soluble in ammonium oxalate. From the solution in $(NH_4)_2C_2O_4$ the zirconium is not precipitated by the addition of dilute HCl (difference from Th).

7. **Ammonium Oxalate** behaves the same as oxalic acid.

From the solution in ammonium oxalate, zirconium is not precipitated on the addition of hydrochloric acid (difference from thorium).

Remark. — A solution of zirconium sulfate behaves quite differently from that of the nitrate and basic chloride towards oxalic acid and ammonium oxalate, a fact which, although published by Berzelius and also by Pfaff, had been entirely forgotten by most chemists until their attention was called to it by R. Ruer.*

On treating an aqueous solution of zirconium sulfate with oxalic acid or ammonium oxalate there is no precipitation; in fact, precipitation will not take place from nitrate or chloride solutions when these contain sufficient sulfuric acid, sodium or ammonium sulfate.

The cause of this different behavior lies in the fact that zirconium forms complex compounds with sulfuric acid and alkali sulfates. Thus the solution of zirconium sulfate contains the acid $H_2[ZrO(SO_4)_2]$, and on treating a solution of the oxychloride or nitrate with sodium or ammonium sulfate (but not the potassium salt) the sodium or ammonium salt of this complex acid is formed:

$$ZrOCl_2 + 2\,Na_2SO_4 = 2\,NaCl + Na_2[ZrO(SO_4)_2].$$

These compounds, however, are electrolytically dissociated in aqueous solution as follows:

$$H_2[ZrO(SO_4)_2] \rightleftarrows 2\,H^+ + [ZrO(SO_4)_2]^{--}.$$

As the zirconium is present in the anion it cannot react with oxalic acid.

8. **Potassium Ferrocyanide** gives a white precipitate in neutral solutions and a greenish-yellow precipitate of zirconium ferrocyanide in acid solutions. Sulfate solutions do not give the precipitation or only to some extent.

9. K_2SO_4. — A cold, concentrated solution of K_2SO_4 precipitates little by little all of the zirconium as potassium zirconium sulfate, insoluble in an excess of the reagent (difference from Al and Be). The precipitate, when produced in the cold, dissolves readily in considerable dilute HCl. If it is produced from a boiling solution, basic zirconium sulfate is formed by hydrolysis, which is quite insoluble in dilute HCl (difference from Th and Ce).

10. Na_2SO_4 produces no precipitation, even on boiling a solution which is slightly acid with sulfuric acid (difference from Ti).

11. H_2O_2 precipitates from slightly acid solutions white, voluminous zirconium peroxide, Zr_2O_5, which evolves chlorine on being warmed with concentrated HCl.

12. $Na_2S_2O_3$ precipitates zirconium completely as the hydroxide, the precipitate being always contaminated with sulfur.

13. **Turmeric Paper,** after being moistened with the hydrochloric acid solution of a zirconium salt and dried, is colored reddish-brown (difference from Th).

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* *Z. anorg. Chem.*, **42**, 85 (1904).

14. **HCl.**—Ruer * recommends the following test for the identification of zirconium:

Precipitate the zirconium in the cold by ammonia, filter, wash, and separate it from the filter as completely as possible. Dissolve the precipitate in hydrochloric acid, or if small in amount treat the paper and precipitate together with not too strong HCl and filter. Evaporate the hydrochloric acid solution to dryness on the water-bath and take up the residue in a little water. To the cold, saturated solution add hydrochloric acid drop by drop; the presence of zirconium will be indicated by the formation of a voluminous precipitate of zirconium oxychloride. Redissolve the precipitate by heating the solution, and allow the liquid to cool. After some time fine, silky needles of $ZrOCl_2 \cdot 8\,H_2O$ will precipitate.

In the somewhat unusual case that zirconium is present in the form of the insoluble meta-zirconic acid, transform the latter into zirconium sulfate by heating with concentrated sulfuric acid (2 : 1), dissolve this in water, precipitate the zirconium by ammonia, and carry out the above process.

15. **Sodium Iodate** produces in slightly acid solutions a voluminous white precipitate of zirconium iodate which is soluble in hot, dilute hydrochloric acid (best method of separating zirconium from aluminium).

16. **Hydrofluoric Acid** as a rule produces no precipitation (difference from thorium, cerium and other rare earths). From concentrated zirconium solutions a voluminous precipitate may be obtained by the careful addition of hydrofluoric acid, but the precipitate is soluble in an excess of the reagent.

Reactions in the Dry Way

ZrO_2 is infusible in the oxyhydrogen flame (difference from the other earths), but glows brightly.

THORIUM, Th. At. Wt. 232.4. Sp. Gr. 11.0. M. Pt. about 1700°.

Occurrence.—Thorite (orangite), $ThSiO_4$, with 50 to 58 per cent ThO_2; thorianite, a mineral discovered in Ceylon, with 72 to 76 per cent ThO_2 and 11 to 12 per cent UO_2.† Small quantities, up to about 8 per cent, of ThO_2 are found with gadolinite, $Y_2O_3 \cdot 3(BeFe)O \cdot 2SiO_2$, monazite, $(Ce,La,Di,)PO_4$, and in the rare niobates, samarskite, pyrochlore, euxenite, etc. Euxenite is essentially a titanate and niobite of Ce(La,Di) and usually contains UO_2 and FeO. Thorite, monazite, and gadolinite are decomposed by acids, preferably sulfuric acid.

The impure metal itself has been obtained by heating $ThCl_4$ or K_2ThCl_6 with metallic sodium. In the air it is stable and exhibits

* *Z. anorg. Chem.*, **42**, 85 (1904).

† *Chem.-Ztg. Rep.*, **1905**, 91.

radio-activity. Upon gentle heating it ignites and burns to the dioxide. The metal dissolves in hydrochloric acid with evolution of hydrogen, it is less readily dissolved by sulfuric acid and by hydrofluoric acid and is practically insoluble in alkali hydroxide solutions.

The dioxide, thoria, is white when pure but is usually gray; upon being heated it becomes bluish, if free from cerium, and luminous. The presence of cerium causes a white light from the glowing oxide.

Ignited thorium dioxide, ThO_2, can be dissolved by fuming with concentrated sulfuric acid, cooling and adding the acid to ice-cold water, or to dilute sulfuric acid; it is not soluble in other acids even after fusing with alkalies. Thorium shows a tendency to form colloidal solutions but less tendency to form complex ions than does cerium, zirconium or titanium.

Reactions in the Wet Way

A solution of $Th(SO_4)_2$ should be used.

1. **$(NH_4)OH$**, **$(NH_4)_2S$**, or **KOH** produces a white precipitate of $Th(OH)_4$, insoluble in an excess of the reagent, but readily soluble in dilute acids when freshly precipitated. By boiling with thorium nitrate, or by treatment with a little aluminium chloride, ferric chloride or hydrochloric acid, it is easy to obtain a colloidal solution of thorium hydroxide. Similarly by dialysis of thorium salts in pure water, it is easy to obtain a colloidal solution of the hydroxide. By igniting the hydroxide, ThO_2 is obtained, which is soluble in concentrated sulfuric acid only after long digestion.

2. **K_2CO_3** or **Na_2CO_3** precipitates the white carbonate, soluble in an excess of the reagent, and not reprecipitated by the addition of ammonia. On boiling, the solution becomes turbid, but clears again on cooling.

3. **$(NH_4)_2CO_3$** precipitates the white carbonate, readily soluble in an excess; on warming to 50° a basic carbonate is precipitated, which redissolves on cooling the solution. Ammonia causes no precipitation in this solution.

4. **$BaCO_3$** completely precipitates thorium salts in the cold.

5. **K_2SO_4** precipitates $K_4Th(SO_4)_4 + 2\,H_2O$, difficultly soluble in water and insoluble in concentrated K_2SO_4 solution (difference from Y). The corresponding sodium compound is readily soluble in water.

6. **Oxalic Acid** precipitates, from solutions which are not too acid, all of the thorium as white, crystalline oxalate, practically insoluble in oxalic and dilute mineral acids.

The precipitate has the formula: $Th(C_2O_4)_2 . 6\,H_2O$. It dissolves in ammonium acetate solutions containing a little free acetic acid. At the boiling temperature

it dissolves in concentrated alkali oxalate solutions, particularly in ammonium oxalate, forming very stable complex ions: $[Th(C_2O_4)_4]^{=\!=}$, $[Th(C_2O_4)_3]^{--}$, or $[Th_3(C_2O_4)_5]^{--}$. On cooling no precipitation takes place if sufficient ammonium oxalate were used. (Difference from the ions of the Ce, La, Pr, Nd and somewhat different from Y and Er.) The addition of hydrochloric acid causes the decomposition of the complex oxalate ion and thorium oxalate is reprecipitated.

By gently igniting the oxalate, thorium dioxide is obtained and will give a colloidal solution with hydrochloric or nitric acid; the *sole* appears milky white by reflected light and a clear, yellow solution by transmitted light (looking through it).

Neutral, anhydrous thorium sulfate dissolves in ice water but on heating, or even on standing at room temperature, it crystallizes out in the hydrated and difficultly soluble condition. (Difference from Al, Be, Yt, Er, Ti, Zr, Ce, Pr and Nd.) This behavior can be used for separating thorium from other rare earths. In boiling water the salt loses its water of crystallization and is then soluble in cold water.

7. **Ammonium Oxalate** likewise precipitates thorium oxalate, which dissolves on boiling with a large excess of this reagent. The solution remains clear after cooling, provided the original solution did not contain too much free sulfuric acid, and enough ammonium oxalate was used. From the boiling solution of the ammonium double oxalate, HCl precipitates practically all of the thorium as oxalate (difference from Zr).

In the presence of ammonium acetate, ammonium oxalate produces no precipitation; but by the addition of HCl almost all of the thorium will be precipitated as oxalate.

8. **HF** produces a white, gelatinous precipitate, which soon changes to a heavy powder. KF causes the same reaction.

9. **$Na_2S_2O_3$** precipitates all of the thorium on boiling.

10. **Potassium Hydroxide** and **Chlorine** do not dissolve thoria.

11. **Potassium Ferrocyanide** gives a white precipitate in neutral or faintly acid solutions; in the former case the test is sensitive.

12. **Potassium Azide,** KN_3, gives in faintly acid solutions a precipitate of hydroxide or of basic thorium azide with evolution of hydrazoic acid:

$$Th^{++++} + 4\,N_3^- + 4\,H_2O \rightarrow \mathbf{Th(OH)_4} + 4\,HN_3.$$

According to Dennis * this is a characteristic reaction of thorium but according to Curtius † zirconium also gives the test in the cold and yttrium on boiling.

13. **Iodic Acid** in nitric acid solutions gives a white, crystalline precipitate of thorium iodate. The reaction is sensitive and other rare earth iodates, being more soluble in nitric acid, can be dissolved

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* *Z. anal. Chem.*, **34**, 82.

† *Ibid.*, **38**, 49.

by treatment with a hot solution of 4 g. KIO_3 in 100 cc. of 6-normal nitric acid and 400 cc. of water.

14. **Hydrogen Peroxide** added to a hot, neutral solution, or to one which is faintly acid with sulfuric acid, or even to an ammonium carbonate solution, precipitates all of the thorium as white, hydrated thorium peroxide.

15. **Sodium Hypophosphate,** $NaHPO_3$, produces a white, flocculent precipitate of thorium hypophosphite by boiling in the presence of considerable hydrochloric acid.

There are no characteristic dry reactions.

THE GADOLINITE EARTH METALS

SCANDIUM, Sc., At. Wt. 45.1; YTTRIUM, Y, At. Wt. 89.3; EUROPIUM, Eu, At. Wt. 152.0; GADOLINIUM, Gd, At. Wt. 157.3; TERBIUM, Tb, At. Wt. 159.2; DYSPROSIUM, Dy, At. Wt. 162.5; HOLMIUM, Ho, At. Wt. 163.5; ERBIUM, Er, At. Wt. 167.7; THULIUM, Tm, At. Wt. 168.5; YTTERBIUM, Yb, At. Wt. 173.5; LUTECIUM, Lu, At. Wt. 175.0

The gadolinite metals, or yttrium earths, constitute a group of trivalent elements that occur as silicates in the minerals gadolinite and rowlandite, as phosphates in xenotime, and as niobates in euxenite, yttrotantalite and certain other rare minerals. In these minerals the elements scandium, yttrium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutecium preponderate over certain other rare elements that occur with them and which are markedly different in their chemical behavior, namely the *cerite metals*. Of all the elements in the group, yttrium and then erbium occur in the largest quantities and may be regarded as the two most important elements. Scandium, however, is also quite widely distributed and has been found recently in certain tungsten and tin ores. The remaining elements are extremely rare in occurrence. Because of their rarity and the difficulties encountered in purifying them it is by no means certain that each of the yttrium earths named actually represents a simple substance or element. In occurrence and chemical properties europium, gadolinium and terbium are very similar, so are dysprosium, holmium, erbium and thulium as well as ytterbium and lutecium. It is beyond the scope of this book to attempt to discuss all of these elements in detail but the typical reactions of yttrium will be given and some of the important differences from the other elements of the group will be pointed out.

Occurrence. — Yttrium is an important constituent of gadolinite, $Y_2O_3 \cdot 3\,(Be,Fe)O \cdot 2\,SiO_2$ and of yttrotantalite $Y_4[(Nb,Ta)_2O_7]_3$ an isomorphous mixture of yttrium pyrotantalate and pyroniobate. The elements of this group are also found in cerite, thorite, and monazite.

Yttrium itself has not been obtained perfectly pure. In the impure state it is a gray powder capable of being polished. It has a high melting point and burns to the oxide. It can be prepared by the electrolysis of fused sodium yttrium chloride or by the reduction with metallic magnesium.

Yttrium oxide, Y_2O_3, is white when pure but yellow when contaminated with other oxides of the group.

The color of the oxides and salts often helps to identify these elements. Thus erbium oxide is pink and so are the solutions of its salts. Europium salts are slightly pink but salts of holmium are

distinctly so. Salts of dysprosium and thulium are light green or bluish green. The oxides and salts of the remaining metals are white or colorless.

The hydroxides of the yttrium earths are bases whose strengths lie between that of the alkaline earth and aluminium groups; yttrium is the most basic and probably the others can be grouped in the following order, — gadolinium, terbium, erbium, ytterbium, . . . scandium. Owing to the somewhat different position in the periodic table, it is probable that the elements between the yttrium and scandium are more closely related to one another and for the same reason scandium in some respects is similar to beryllium and in other respects to thorium and zirconium. In the fractional precipitation by bases or in the decomposition of the nitrates by ignition, the elements show the same gradation of properties, — yttrium is always the last to precipitate and the last to decompose. Its separation from the other yttrium earths is usually based upon the fact that the last fractions are invariably rich in yttrium. The only element of the group known to give an oxide higher than that of the trivalent metal appears to be terbium, which has the oxide Tb_4O_7, a black substance when pure but causing other oxides of the group to appear yellow when it is present in small quantities. Heated in the non-luminous flame, yttrium oxide glows with a white light and erbium oxide gives a strong green light.

Excepting scandium, the salts of these metals are not readily hydrolyzed even when the acid is weak. The tendency to form complex salts is less than that of thorium and zirconium but greater than that of the cerite earths. Particularly important for separating yttrium earths from cerite earths is the greater solubility of the double sulfates. It is difficult to obtain double nitrates at ordinary temperatures. The chlorides crystallize with six molecules of water and when heated to 120° lose water and hydrochloric acid and are converted into insoluble basic chlorides of the YOCl type. The chlorides are more soluble in pyridine than are the chlorides of the cerite metals. The anhydrous chlorides are not easily volatilized but yttrium and scandium form the most volatile chlorides of the group.

Reactions in the Wet Way

A solution of $Y(NO_3)_3$ should be used.

Yttrium	Other Yttrium Earths
1. **NH_4OH** and **$(NH_4)_2S$** precipitate the white hydroxide, insoluble in an excess. In the presence of tartaric or citric acid no hydroxide is precipitated but the addition of ammonium hydroxide to a tartaric acid solution causes the formation of a white flocculent precipitate of ammonium double tartrate.	Behave like yttrium.
2. **KOH** and **NaOH** precipitate the white hydroxide, insoluble in an excess; the presence of tartaric acid does not prevent precipitation, but in this case yttrium tartrate is precipitated (difference from Al, Be, Th, and Zr). On igniting the precipitate, the oxide is obtained, which is readily soluble in acids. The hydroxides precipitated from hot solutions are gelatinous but easy to filter; from cold solutions they are slimy and hard to wash. The hydroxides of yttrium and of erbium absorb carbon dioxide from the air.	Behave like yttrium. According to v. Panayeff, erbium ions do not react quite the same.
3. **$(NH_4)_2CO_3$** produces a white precipitate of the carbonate, readily soluble in an excess of the reagent; after standing some time the solution becomes turbid, owing to the deposition of a double salt, $Y_2(CO_3)_3 \cdot 2\,(NH_4)_2CO_3 \cdot 2\,H_2O$. The solution of the pure hydroxide dissolved in excess of ammonium carbonate gives complete	With erbium the solution does not become turbid on standing.

Yttrium	Other Yttrium Earths
precipitation upon boiling but if ammonium chloride is present it serves to decompose the precipitate upon further boiling, with liberation of ammonia, and the yttrium goes back into solution.	
4. **K_2CO_3** and **Na_2CO_3** precipitate the white carbonate, readily soluble in excess; after standing some time an insoluble double salt separates out.	Erbium behaves like yttrium, only the solution does not become turbid on standing.
The solubility of the carbonate in excess of the precipitant is much greater than that of the cerite earths and this serves as a basis of separation. Yttrium carbonate dissolves more readily in potassium bicarbonate and in ammonium carbonate than in normal potassium carbonate but the solubility is not as great as that of the corresponding beryllium precipitate.	
5. **$BaCO_3$** does not precipitate yttrium in the cold, and only incompletely on warming.	Erbium is not precipitated at all, even on warming.
6. **Oxalic acid** precipitates white yttrium oxalate, insoluble in an excess, difficultly soluble in HCl, and perceptibly soluble in ammonium oxalate.	In erbium solutions, oxalic acid produces a light-red, pulverulent precipitate; otherwise the reaction is the same as with yttrium. This is an important characteristic of the entire group of rare earths (except zirconium) which serves to distinguish them from aluminium and beryllium. The solubility of the yttrium earth oxalates is, in general, greater than that of the cerite earths and, by boiling with concentrated alkali oxalate, the yttrium earth

Yttrium	Other Yttrium Earths
	oxalates, particularly scandium oxalate, dissolve more readily than do the oxalates of the cerite group; upon diluting and cooling there is usually complete reprecipitation (difference from thorium).
7. K_2SO_4 forms a double salt which is soluble in K_2SO_4 solution (difference from Zr, Th, Ce, La, and Di).	Behave like yttrium. (Difference from thorium, zirconium and the cerite metals.) Within the group of yttrium earths (disregarding the very slightly soluble scandium double sulfate) the double sulfate of terbium is the least soluble; it occupies a position intermediate between the cerite earths and the other yttrium earths.
8. **HF** produces white amorphous YF_3, which becomes pulverulent on warming, and is insoluble in water and in HF (difference from Al, Be, Ur and Ti). The precipitate is soluble in mineral acids if it has not been ignited; after strong heating it is less soluble.	Scandium fluoride is not dissolved much by concentrated hydrochloric acid and after being ignited it requires concentrated sulfuric acid to attack it. Scandium fluoride, like zirconium fluoride, forms easily soluble double fluoride and thus differs from the other rare earth fluorides.
9. $Na_2S_2O_3$ does not cause precipitation.	Scandium is the only member of the group to behave like aluminium, thorium and titanium.
10. H_2O_2 in alkaline solution causes the formation of gelatinous, very unstable hydrated peroxides of the general formula, — $R(O \cdot OH)(OH)_2$. Yttrium solutions do not give an absorption spectrum.	

Yttrium	Other Yttrium Earths
11. HIO_3 does not give a precipitate which is insoluble in nitric acid (difference from thorium).	
12. $NaHPO_3 \cdot 2\ H_2O$ does not give a precipitate in strong hydrochloric acid solutions (difference from thorium).	
	The absorption spectra are especially important in the examination of this group of metals, furnishing, in fact, about the only means of controlling the purification by fractionation. The most important bands for erbium lie at 653, **523, 487, 450** and 442; for dysprosium at 753, 475, 451.5, 427.5.

Reactions in the Dry Way

Yttrium oxide is strongly luminous on being heated; otherwise there is no reaction.	Erbium oxide, on being heated on a platinum wire, colors the flame distinctly green. If the light is viewed through a spectroscope, a number of bright lines will be seen in the dark green which coincide with the dark lines obtained in the absorption spectrum.

THE CERITE METALS

CERIUM, Ce, At. Wt. 140.25, M. Pt. 623°; LANTHANUM, La, At. Wt. 139.0, M. Pt. 810°; PRASEODYMIUM, Pr, At. Wt. 140.9, M. Pt. 940°; NEODYMIUM, Nd, At. Wt. 144.3, M. Pt. 840°; SAMARIUM, Sa, At. Wt. 150.4, M. Pt. 1300–1400°

The elements of this group all occur in small quantities (excepting cerium) in the minerals mentioned on page 512 which contain larger quantities of the yttrium earths. They occur in larger quantities as silicates in the minerals cerite, $H_8Ca(CeAl)_2Si_3O_{13}$, and orthite (allanite), $HCa_2Ce_3Si_3O_{13}$, as phosphate in monazite, as niobate and tantalate in æschynite as fluoride in fluorcerite and in a number of rarer minerals of similar composition. Cerium is the most common and most important element of the group but all the members are better known than most of the yttrium group elements.

The best way of attacking the minerals is by treatment with concentrated sulfuric acid. The silicates cerite, orthite and gadolinite can be decomposed by repeated evaporation with strong hydrochloric acid. The phosphates (monazite, xenotime, etc.), are not decomposed well by hydrochloric acid; after heating with concentrated sulfuric acid, the excess of the acid should be volatilized and the moist mass stirred slowly into ice water. The niobates, tantalates and titanates (fergusonite, euxenite, æschynite, etc.), are best fused with five or six times as much sodium acid sulfate; after cooling the melt, a few drops of concentrated acid are added to replace that lost by volatilization and the solid is then treated with water which causes the separation of niobic and tantalic acids. Hydrofluoric acid also is useful in attacking most of these minerals (except niobates and tantalates), the action taking place even when cold; the earth acids go into solution and the earth fluorides are left undissolved.

The metals themselves are obtained by electrolysis of the fused chlorides or fluorides. They are white or pale yellow and fairly stable in the air. The specific gravity lies between 6.15 (lanthanum) and 7.7 (samarium), that of cerium being 7.04. They are good reducing agents and have been used as such in place of metallic magnesium.

Metallic cerium is strongly pyrophoric; it gives sparks when struck or rubbed against steel. A pyrophoric alloy of cerium and iron is used in gas lighters. The metals all burn in oxygen and give a bright light. They decompose water slowly and dissolve readily in acid with liberation of hydrogen.

A mixture of the oxides, as obtained by ignition of the oxalates from one of the typical minerals, has a brownish-red color and may be regarded as containing salts of the trivalent metals with quadrivalent cerium as acidic constituent, the latter being the only member of the group which is known to form a stable oxide or salt that contains other than trivalent metal. At higher temperatures the oxides become crystalline and at the temperature of the electric arc they are slightly volatile. The oxides dissolve in acid more readily than do the oxides of the yttrium series, and although the solubility is affected by the previous treatment, the ignited oxides dissolve in

acid unless more than 40 or 50 per cent of ceric oxide, CeO_2, is present. The cerite earths form strong bases and set free ammonia from ammonium salts even when cold. Lanthanum hydroxide is about as basic as calcium hydroxide but the basicity decreases in the following order, — trivalent cerium, praseodymium, neodymium, samarium. Quadrivalent cerium forms an amphoteric hydroxide and its basicity lies between that of the hydroxides of zirconium and thorium.

The chlorides of these trivalent elements usually crystallize with six molecules of water; praseodymium chloride, however, has seven molecules of water of crystallization. The nitrates also crystallize with six molecules of water. They form double salts of the type, $R(NO_3)_3 \cdot 2\,NH_4NO_3 \cdot 4\,H_2O$; the stability and insolubility of the salt decreases with rise in atomic weight from lanthanum to samarium. Upon heating the chlorides or nitrates, insoluble basic salts, ROX, are formed (difference from yttrium earths); the salts of the metals with low atomic weight are the most stable.

The sulfates crystallize with four, eight, or twelve molecules of water. Heating them to 400° or 500° causes the formation of anhydrous sulfates which form strongly supersaturated solutions in cold water but rise of temperature lowers the solubility; this property is utilized in separating the members of this group and of the very similar yttrium earths from other elements.

The carbonates react with concentrated alkali carbonate solutions to form difficultly-soluble double salts; the potassium compounds being more soluble than the sodium or ammonium ones. Dilution causes precipitation of the carbonates, lanthanum carbonate being precipitated first, then praseodymium, cerium and neodymium.

The oxalates are practically insoluble in oxalic acid, but somewhat soluble in mineral acid; the most basic element, lanthanum, gives the oxalate most readily dissolved.

CERIUM

Cerium forms two oxides, Ce_2O_3 and CeO_2; the former is basic and the latter is amphoteric. The cerous salts are white, while the ceric salts are orange red. The solutions are colorless and have a sweet but astringent taste.

Reactions in the Wet Way

1. Cerous Salts

A solution of cerous nitrate, $Ce(NO_3)_3$, should be used.

1. **NH_4OH** and **$(NH_4)_2S$** each produces a white precipitate of $Ce(OH)_3$, insoluble in an excess of the reagent, but readily soluble in acids. In the presence of tartaric and citric acids, etc., the above reagents cause no precipitation (difference from Y).

2. **NaOH** or **KOH** also precipitates white $Ce(OH)_3$, even in the presence of tartaric acid, etc. The white $Ce(OH)_3$ becomes yellow gradually on standing in the air, on account of being oxidized to $Ce(OH)_4$.

3. **K_2CO_3** or **$(NH_4)_2CO_3$** produces a white precipitate insoluble in an excess of the reagent. The precipitate is amorphous at first but gradually becomes crystalline. In concentrated solutions of alkali carbonates, very slightly soluble double salts are formed, the potassium salt being the most soluble.

4. **Oxalic Acid** or **Ammonium Oxalate** precipitates white cerous oxalate, insoluble in an excess of the reagent, and in dilute mineral acids. On ignition, pale yellow, insoluble CeO_2 is formed.* If the oxalate is contaminated with praseodymium oxalate, a cinnamon-colored oxide is obtained, which is perfectly soluble in dilute acids.

5. **$BaCO_3$** slowly precipitates cerium in the cold and more rapidly in a hot solution.

6. **K_2SO_4**. If a *neutral* solution of cerous salt is treated with solid K_2SO_4 until no more will dissolve, a crystalline precipitate of $Ce_2(SO_4)_3 \cdot 3\ K_2SO_4$ is slowly formed at room temperature, or more quickly on heating. All of the cerium can be precipitated in this way, as the double sulfate is insoluble in concentrated potassium sulfate solution, but it will dissolve in considerable pure water or more readily in acids. From slightly *acid* solutions cerium can be completely precipitated with K_2SO_4 as $Ce_2(SO_4)_3 \cdot 2\ K_2SO_4 \cdot 2\ H_2O$. (Difference from Al, Be and yttrium earths.)

Na_2SO_4 behaves similarly (difference from Th and Zr).

7. **HF** produces in neutral and slightly acid solutions of cerous salts a gelatinous precipitate which by long digestion with the hot solution gradually becomes pulverulent. The precipitate of $CeF_3 \cdot H_2O$ is practically insoluble in water and dilute hydrofluoric acid, but readily soluble in other mineral acids (difference from Al, Be, Zr and Ti).

8. **H_2O_2** colors neutral cerous solutions yellow, but after adding an acid the color disappears, as the cerium peroxide is reduced to cerous salt by hydrogen peroxide and acid. If a cerous salt is treated with a slight excess of ammonium hydroxide and then with H_2O_2; the precipitate becomes reddish orange in color, something like $Fe(OH)_3$. This is the most sensitive test for cerium; it was discovered by Lecoq de Boisbaudran. The composition of the precipitate has been given as $CeO_2 \cdot Ce_2O_3 \cdot H_2O_2$ and as $Ce(OH)_3O_2H$.

If air is led through a solution of cerous ions to which concentrated potassium carbonate has been added, the deep red color of cerium peroxide is formed; boiling the solution or shaking with a reducing agent, such as arsenious acid, causes precipitation of ceric hydroxide, $Ce(OH)_4$.

* Only when the cerous oxalate is pure. If it contains traces of praseodymium, the CeO_2 is obtained as a bright-yellow powder.

9. **Chlorine.** — If a cerous salt is treated with an excess of alkali hydroxide and then with chlorine gas, a yellow precipitate of $CeO_2 \cdot 3\ H_2O$ is obtained. If the chlorine gas is passed through the solution for a long time, the precipitate will redissolve.

10. **Bromine** behaves like chlorine except that an excess of this oxidizing agent does not dissolve the precipitate. (Difference from lanthanum and didymium.)

11. Cerous salts may be oxidized to ceric salts in acid solutions (*a*) by heating with PbO_2 and HNO_3 (1 : 2); (*b*) by heating with ammonium persulfate; (*c*) by electrolysis. In all cases, the solution becomes yellow or orange in color.

12. $Na_2S_2O_3$ gives no precipitate even in concentrated solutions of cerous salts.

2. Ceric Salts

A solution of either ceric nitrate, $Ce(NO_3)_4$, or of ceric ammonium nitrate, $Ce(NO_3)_4 \cdot 2\ NH_4NO_3 + H_2O$, should be used.

The beautiful orange-red color of these solutions is characteristic of all ceric salts, as is also their tendency to form difficultly soluble basic salts.

Preparation of Ceric Compounds. — As has been already stated, cerous hydroxide on standing in the air gradually turns yellow, on account of the formation of ceric hydroxide. This oxidation takes place immediately on the addition of chlorine or hypochlorite. If the solution of a cerous salt is treated with caustic potash solution and chlorine is conducted into it, the white cerous hydroxide which was at first formed is quickly changed to light-yellow ceric hydroxide. The latter compound dissolves in dilute acids, forming orange solutions. It dissolves in concentrated hydrochloric acid with evolution of chlorine, forming *cerous* chloride. If white cerous hydroxide is heated in the air, it loses water and is changed into CeO_2, which is nearly white when cold, dark orange when hot, and is almost entirely insoluble in concentrated hydrochloric and nitric acids. In the presence of reducing substances (such as KI, $FeSO_4$, etc.) it dissolves in acids, forming cerous salts:

$$2\ CeO_2 + 8\ HCl + 2\ KI = 2\ KCl + 4\ H_2O + I_2 + 2\ CeCl_3.$$

CeO_2 can also be dissolved by warming with concentrated sulfuric acid, with evolution of oxygen and formation of cerous sulfate. It can be readily brought into solution by fusing with potassium pyrosulfate and dissolving the melt in considerable hot water to which a little acid is added.

If a mixture of cerous and praseodymium hydroxides is ignited in the air, a cinnamon-colored mass is obtained, which contains all of the cerium as dioxide and is readily soluble in dilute acids, forming ceric salts. If concentrated HCl is used, there is an evolution of chlorine, the ceric salt being reduced to cerous chloride. Concentrated nitric acid dissolves it, forming cerous and ceric salts; a distinct evolution of oxygen can always be detected.

The reason why the brown mass containing a little praseodymium dissolves although the pure oxide does not, is probably the following: CeO_2, like MnO_2 and

PbO_2 (see pp. 171 and 218), plays the part of an acid anhydride, so that the brown mass contains the praseodymium as the salt of ceric acid. On treating this salt with a stronger acid, the praseodymium salt of the latter is formed, setting free ceric acid (ceric hydroxide), which in the hydrated form is readily soluble in acids, forming ceric salts.

Basic Ceric Salts. — If a solution of ceric nitrate is evaporated on the water-bath to a consistency of syrup, the mass dissolves readily in water after it has become cold, and the solution can be boiled without becoming turbid. If, however, a little nitric acid is added, a yellow precipitate is immediately formed, consisting of basic ceric nitrate; on the addition of more acid the precipitate redissolves. This can be explained as follows: By treating the solution of ceric nitrate with considerable water it becomes hydrolyzed considerably, but the basic salt produced is present in the *hydrosole* state and is changed by the acid into the *hydrogele* form.

As lanthanum and didymium salts do not yield basic salts under these conditions, this property can be used for separating cerium from these metals.

It is characteristic of cerium to form with ammonium nitrate an easily crystallizable salt, ceric ammonium nitrate: $Ce(NO_3)_4 \cdot 2\,NH_4NO_3 \cdot H_2O$.

All ceric salts may be readily reduced by the ordinary reducing agents (alcohol, HI, SO_2, H_2S, HNO_2, H_2O_2, etc.), to cerous salts.

1. **NaOH, KOH** or **NH_4OH** precipitates yellow, shiny ceric hydroxide, $Ce(OH)_4$. It dissolves in nitric acid giving a red solution but with hydrochloric acid chlorine is evolved and cerous chloride is formed

$$2\,Ce(OH)_4 + 8\,H^+ + 2\,Cl^- \rightarrow 2\,Ce^{+++} + Cl_2\uparrow + 8\,H_2O$$

Ceric hydroxide is a weak base and ceric salts are unstable and easily reduced in acid solutions. Ceric chloride is known only in solution and it decomposes easily like manganic chloride.

Ceric hydroxide dissolves in sulfuric acid giving a mixture of cerous and ceric sulfates. Dry ceric sulfate is known and crystals of it with four molecules of water can be obtained but heating in sulfuric acid solutions causes decomposition:

$$4\,Ce(SO_4)_2 + 2\,H_2O \rightarrow 2\,Ce_2(SO_4)_3 + 2\,H_2SO_4 + O_2\uparrow.$$

2. **Oxalic Acid** added to a concentrated solution of a ceric salt at first precipitates a dirty orange precipitate which gradually becomes yellow and gelatinous as the addition of oxalic acid is continued, and finally crystalline. The precipitate dissolves in a large excess of oxalic acid, but the solution gradually becomes turbid in the cold, or more quickly on heating, as the ceric salt is reduced to cerous salt at the expense of the oxalic acid from which carbon dioxide is evolved. Finally all the cerium will be precipitated as cerous oxalate. (Difference from La, Di and the yttrium earths.)

Ammonium Oxalate behaves similarly.

3. **Ammonium Nitrate** in concentrated nitric acid solution gives a relatively insoluble double nitrate, $Ce(NH_4)_2(NO_3)_6$. The other cerite metals form more soluble double nitrates.

4. **Hydrogen Peroxide** reduces acid solutions of ceric salts:

$$2\,Ce^{++++} + H_2O_2 \rightarrow 2\,Ce^{+++} + 2\,H^+ + O_2\uparrow.$$

Reactions in the Dry Way

The borax bead is colored dark brown when hot and light yellow to colorless when cold, after being heated in the oxidizing flame. In the reducing flame the bead becomes colorless, although strongly ignited CeO_2 will remain suspended in the bead, giving it a turbid yellowish appearance.

LANTHANUM, La. At. Wt. 139.0. M. Pt. 810°?

Lanthanum forms only one oxide,* La_2O_3, which, even after being strongly ignited, dissolves readily in acids. Its salts are colorless and yield no absorption spectrum, so that lanthanum may be distinguished in this way from didymium and erbium. The arc spectrum however shows characteristic lines in the violet and ultra-violet part. It is the most basic of the cerite earths. The oxide is white when pure and resembles calcium oxide (lime) in its behavior toward water and toward carbon dioxide. The sulfate, $La_2(SO_4)_3 \cdot 9\ H_2O$, is practically insoluble in water at 20° to 30° but dissolves in ice water. The salts are colorless.

Reactions in the Wet Way

A solution of lanthanum nitrate, $La(NO_3)_3$, should be used.

1. **NH_4OH** and **$(NH_4)_2S$** precipitate a white basic salt which is difficult to filter. The presence of tartaric acid prevents the precipitation. (Difference from yttrium.)

2. **KOH** and **NaOH** precipitate the white hydroxide, **$La(OH)_3$**. There is no change to be noticed on treating with oxidizing agents (difference from Ce). $La(OH)_3$ is soluble enough in water to turn red litmus-paper blue, and it decomposes ammonium salts on warming with evolution of ammonia. The fused oxide is readily soluble in acids.

3. **$(NH_4)_2CO_3$** produces a white precipitate slightly soluble in an excess of the reagent (difference from aluminium); after standing some time crystalline lanthanum ammonium carbonate is precipitated.

$BaCO_3$ causes complete precipitation of lanthanum.

4. **Oxalic Acid** produces a white crystalline precipitate, insoluble in an excess of the precipitant and in ammonium oxalate, but soluble in dilute mineral acids. (Difference from Th.)

5. **K_2SO_4** precipitates white, crystalline $La_2(SO_4)_3 \cdot 3\ K_2SO_4$, insoluble in a concentrated K_2SO_4 solution. (Continued on p. 530.)

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* H_2O_2 is said to cause the formation of La_2O_5. *Cf. Z. anorg. Chem.*, **21**, 70 (1899).

SUMMARY OF THE REACTIONS OF THE RARE EARTHS

	KOH or NaOH	NH_4OH or $(NH_4)_2S$	K_2CO_3 or Na_2CO_3*	$(NH_4)_2CO_3$	$Na_2S_2O_3$
Al_2O_3	White precipitate soluble in excess. Tartaric acid prevents the precipitation.	White precipitate insoluble in excess.	White precipitate insoluble in excess.	White precipitate insoluble in excess.	White precipitate on boiling the almost neutral solution.
BeO	White precipitate soluble in excess, reprecipitated on boiling or diluting. Tartaric acid prevents the precipitation.	White precipitate insoluble in excess.	White precipitate very difficulty soluble in a large excess.	White precipitate readily soluble in excess and reprecipitated on boiling.†	No precipitate.
ZrO_2	White precipitate insoluble in excess. Tartaric acid prevents the precipitation.	White precipitate insoluble in excess.	White precipitate slightly soluble in excess, but reprecipitated by NH_4OH.	White precipitate soluble in large excess, but reprecipitated on boiling.	White precipitate (mixed with sulfur) on boiling.
ThO_2	White precipitate insoluble in excess. Tartaric acid prevents the precipitation.	White precipitate insoluble in excess. It is precipitated before the cerite metals.	White precipitate soluble in excess, and not reprecipitated by addition of NH_4OH. The solution becomes turbid on boiling, but clears on cooling.	Behaves as with K_2CO_3.	Almost completely precipitated on boiling.
Y_2O_3	White precipitate insoluble in excess. Tartaric acid does not prevent the precipitation, but yttrium tartrate is then formed.	White precipitate insoluble in excess.	White precipitate soluble in excess. After some hours an insoluble double salt is formed.	Behaves as with K_2CO_3.	No precipitate.

SUMMARY OF THE REACTIONS OF THE RARE EARTHS. — (*Continued.*)

	KOH or NaOH	NH_4OH or $(NH_4)_2S$	K_2CO_3 or Na_2CO_3*	$(NH_4)_2CO_3$	$Na_2S_2O_3$
Er_2O_3	Pink precipitate insoluble in excess. Tartaric acid prevents the precipitation.	Pink precipitate insoluble in excess. Tartaric acid prevents the precipitation.	White precipitate soluble in excess. On boiling, all of the erbium is reprecipitated.	Behaves as with K_2CO_3, except that the precipitate is more soluble in an excess.	No precipitate.
Ce_2O_3	White precipitate insoluble in excess, which is gradually colored yellow on standing in the air. Tartaric acid prevents the precipitation.	Behaves as with KOH. The precipitate becomes orange when treated with H_2O_2.	White precipitate slightly soluble in excess.	Behaves as with K_2CO_3.	No precipitate.
CeO_2	Yellow $Ce(OH)_4$ is precipitated, soluble in HCl with evolution of Cl_2 and formation of cerous chloride. After ignition it becomes insoluble in acids.	Behaves as with KOH.	Yellow precipitate almost entirely insoluble in excess.	Yellow precipitate soluble in considerable excess, but reprecipitated on boiling.	No precipitate.
La_2O_3	White precipitate insoluble in excess. Tartaric acid prevents the precipitation.	Behaves as with KOH. The precipitate produced from an acetic acid solution with dilute ammonia is a basic salt, which becomes blue on treatment with iodine.	White precipitate insoluble in excess.	Behaves as with K_2CO_3.	No precipitate.
Di_2O_3	Violet precipitate insoluble in excess. Tartaric acid prevents the precipitation.	Behaves as with KOH.	Violet precipitate of didymium carbonate, insoluble in excess.	Behaves as with K_2CO_3.	No precipitate.

* Use the double-normal solution: concentrated solutions give precipitates, in nearly every case, soluble in excess of the reagent.
† This reaction is used to separate aluminium from beryllium: the separation is not quantitative.

SUMMARY OF THE REACTIONS OF THE RARE EARTHS. — (*Continued.*)

	Oxalic Acid	$(NH_4)_2C_2O_4$	HF	$BrCO_3$	Absorption Spectrum	K_2SO_4
Al_2O_3	No precipitate.	No precipitate.	No precipitate.	Completely precipitated in the cold.	None.	No precipitate.
BeO	No precipitate.	No precipitate.	No precipitate.	Completely precipitated in the cold.	None.	No precipitate.
ZrO_2	White voluminous precipitate soluble in excess, difficultly soluble in very dilute HCl (cf. p. 506).	White precipitate soluble in excess, and not reprecipitated by addition of considerable HCl.	No precipitate.	No precipitate in the cold. Incompletely precipitated on warming.	None.	A concentrated solution of K_2SO_4 slowly precipitates zirconium potassium sulfate, soluble in considerable dilute HCl unless it was precipitated from a boiling solution, when it is almost insoluble in HCl.
ThO_2	White precipitate insoluble in excess and in dilute mineral acids; soluble in ammonium acetate.	White precipitate soluble in excess on boiling, and not reprecipitated on cooling provided that the original solution did not contain too much free acid. The solution is precipitated by considerable HCl.	No precipitate.	Completely precipitated in the cold.	None.	Precipitates a double salt insoluble in a concentrated K_2SO_4 solution.
Y_2O_3	White precipitate insoluble in excess, and difficultly soluble in dilute HCl.	White precipitate soluble in a large excess.	White, amorphous precipitate insoluble in HF, and insoluble in dilute mineral acids after being ignited.	No precipitation in the cold. Incompletely precipitated on warming.	None.	No precipitation. The double salt is soluble in K_2SO_4 solution.

SUMMARY OF THE REACTIONS OF THE RARE EARTHS. — (*Continued.*)

	Oxalic Acid	$(NH_4)_2C_2O_4$	HF	$BaCO_3$	Absorption Spectrum	K_2SO
Er_2O_3	Pink precipitate insoluble in excess, difficultly soluble in dilute HCl.	Pink precipitate on boiling, scarcely soluble at all.	Pale pink gelatinous precipitate.	No precipitation in the cold, incompletely precipitated on warming.	Characteristic.	No precipitation; the double salt is soluble in K_2SO_4 solution.
Ce_2O_3	White precipitate insoluble in oxalic acids and in dilute mineral acids.	White precipitate insoluble in excess.	White gelatinous precipitate.	Slowly but completely precipitated in the cold.	None.	A double salt is precipitated, insoluble in K_2SO_4 solution.
CeO_2	Brown ceric oxalate is at first precipitated, which on the addition of more oxalic acid is changed to white cerous oxalate with loss of CO_2.	Behaves as with oxalic acid.	Yellowish gelatinous precipitate.	Completely precipitated in the cold.	None.	A double salt is precipitated, insoluble in K_2SO_4 solution.
La_2O_3	White precipitate insoluble in excess.	Same as with oxalic acid. The precipitate is insoluble in $(NH_4)_2C_2O_4$.	White gelatinous precipitate.	Completely precipitated in the cold.	None.	A double salt is precipitated, insoluble in K_2SO_4 solution.
Di_2O_3	Violet precipitate insoluble in excess. The solid salt shows in reflected light the well-known absorption spectrum.	Behaves as with oxalic acid.	Violet gelatinous precipitate.	Completely precipitated in the cold.	Characteristic.	A double salt is precipitated, insoluble in K_2SO_4 solution.

* NOTE— These tables were compiled with the help of those published by C. GLASER, *Chem.-Zeitung*, 1896.

ANALYSIS OF GADOLINITE (CERITE).

Gadolinite may contain: SiO_2, Y_2O_3, Er_2O_3, Ce_2O_3, Di_2O_3, La_2O_3, Fe_2O_3, FeO, BaO, MgO, Na_2O, H_2O, and often some of the metals of the H_2S group.

Treat 2 gms. of the finely divided mineral repeatedly with small portions of conc. HCl, and a little HNO_3, and evaporate to dryness on the water-bath; the mineral is completely decomposed by this treatment. Moisten the dry mass with 5 cc. of conc. HCl, allow the acid to act upon the mass for fifteen minutes, then add 100 cc. of water, and filter off the silicic acid. The metals will be found in the filtrate. Saturate with H_2S, and filter off any metals of the H_2S group. Examine this precipitate according to Table IX, page 289. Boil off the H_2S from the filtrate and then add a boiling solution of oxalic acid little by little while stirring. Filter off the precipitate.

PRECIPITATE: Ce, La, Di, Y, and Er as oxalates.

Wash the precipitate with water, dry, and ignite in a porcelain dish, whereby a cinnamon-colored mass, consisting of a mixture of the oxides of the rare metals is obtained. Dissolve it in as little HNO_3 as possible, add a little alcohol (to reduce ceric salt to cerous), evaporate on the water-bath to dryness, dissolve in a little water, treat with an excess of solid K_2SO_4 and allow to stand over night. In the morning filter off the precipitate and wash it with K_2SO_4 solution.

PRECIPITATE: Ce, La, and Di as $R_2(SO_4)_3 \cdot 3\,K_2SO_4$.

Dissolve the precipitate in very dilute HCl, precipitate with oxalic acid, wash, dry, and ignite. Dissolve the oxides thus formed in a little HCl, carefully precipitate with NaOH (avoiding an excess) saturate the solution with chlorine and filter.

SOLUTION: Y and Er as $R_2(SO_4)_3 \cdot 3\,K_2SO_4$.

Precipitate the solution with oxalic acid, filter, ignite, and dissolve the oxides in a very little HNO_3, evaporate to dryness, dissolve in water and

SOLUTION: Be^{+++}, Al^{+++}, Fe^{++}, Ca^{++}, Mg^{++}, and Na^{+}.

Add $NH_4OH+(NH_4)_2S$ and test the filtrate in the usual way for Mg and Na. Filter off the precipitate (consisting of $Be(OH)_2$, $Al(OH)_3$, FeS, and CaC_2O_4), wash, dry, gently ignite, and then digest with conc. HCl and 1 cc. HNO_3 on the water-bath until completely dissolved. Evaporate off the excess of acid, dissolve the residue in water, add ammonia, and filter off the precipitate. Only calcium now remains in the filtrate, which is precipitated as carbonate and confirmed as usual.

*Dissolve the precipitate (consisting of $Be(OH)_2$, $Al(OH)_3$, and $Fe(OH)_3$) in a little HCl, evaporate almost to dryness, and then treat with an excess of $(NH_4)_2CO_3$ solution, allow to stand fifteen minutes, and filter. In case a precipitate of $Fe(OH)_3$ and $Al(OH)_3$ * is*

PRECIPITATE: $Ce(OH)_4$.	SOLUTION: $LaCl_3+DiCl_3$.
Dissolve the washed precipitate in HNO_3, and treat the yellowish-orange solution with H_2O_2, until it is decolorized; then add a little dilute ammonia. A brown precipitate shows the presence of Ce.	*Acidify with HCl, boil, precipitate with oxalic acid, filter, wash, dry, and ignite the residue. Dissolve the oxides in as little HNO_3 as possible and examine in the spectroscope. The presence of Di is shown by the formation of dark absorption bands.* *To test for La^{+++}, treat the solution with ammonium acetate, precipitate with very dilute ammonia, filter through asbestos, and wash three times with water. Then treat the precipitate with solid iodine, and if La is present a blue color will be noticed in a few minutes.*

examine the solution with the spectroscope; black absorption bands show the presence of Er.
Treat the solution with HF; the formation of a white amorphous precipitate insoluble in HF shows the presence of Y.

obtained, treat the filtrate with a few drops of $(NH_4)_2S$ (to remove the last traces of iron) until no further precipitate of Fe_2S_3 or FeS is formed. Filter and boil the filtrate for some time and again filter.

PRECIPITATE.	SOLUTION.
Basic beryllium carbonate. *Dissolve in HCl, add an excess of KOH, whereby the precipitate at first formed redissolves.* *Dilute the solution with water and boil. A white precipitate shows the presence of Be.*	*Reject.*

* Iron and aluminium are tested for in the usual way.

6. **Lanthanum Sulfate** is soluble only in ice-cold water; on warming the saturated solution to 30° the salt separates out thickly (difference from cerium).

7. **Iodine.** — If ammonia is added to a cold, dilute acetic acid solution of a lanthanum salt, and the slimy precipitate is washed with water and then treated with solid iodine, the whole mass gradually assumes a blue color which is similar to that produced by the action of iodine upon starch (this property is peculiar to lanthanum). The blue color is destroyed by the addition of acids or alkalies, and distinguishes it from all the other earths.

8. **HF** precipitates white gelatinous lanthanum fluoride, which eventually becomes crystalline $LaF_3 \cdot 3\,H_2O$; the precipitate is insoluble in an excess of the precipitant and in dilute acid it is gradually dissolved by strong mineral acids.

9. $Na_2S_2O_3$ does not cause precipitation of lanthanum ions.

DIDYMIUM { **NEODYMIUM, Nd. At. Wt. 144.3. M. Pt. 840°?**
PRASEODYMIUM, Pr. At. Wt. 140.9. M. Pt. 940°?

It is very difficult to separate these two metals from one another. It is accomplished only by repeated fractional crystallization of the ammonium double nitrates.

Neodymium apparently forms only one oxide, Nd_2O_3; it appears bluish after being ignited, and is readily soluble in acids, forming violet salts, which afford a characteristic absorption spectrum.

Praseodymium, on the other hand, forms a greenish-white oxide, Pr_2O_3, which on being ignited is changed into dark-brown peroxide, Pr_4O_7. On being heated in a stream of hydrogen, the latter is reduced back to Pr_2O_3. The peroxide dissolves in acids with loss of oxygen, forming greenish salts corresponding to the lower oxide and yielding a characteristic absorption spectrum.

The **Didymium** reactions take place with a mixture of the two elements. A solution of didymium nitrate, $Di(NO_3)_3$, is used.

Didymium salts are violet and show a characteristic absorption spectrum (difference from Ce and La). The behavior toward NH_4OH, $(NH_4)_2S$, KOH, $(NH_4)_2CO_3$, and K_2SO_4 is exactly the same as with lanthanum. Oxalic acid precipitates the reddish oxalate, which in other respects is like lanthanum oxalate.

Absorption Spectrum of Praseodymium. — 596.9$\mu\mu$, 590.4$\mu\mu$, **482.1**$\mu\mu$, **469.5**$\mu\mu$, and **444.1**$\mu\mu$.

Absorption Spectrum of Neodymium. — **729.1**$\mu\mu$, 690.6$\mu\mu$, (**579.7**$\mu\mu$, **575.9**$\mu\mu$), 531.7$\mu\mu$, (**522.2**$\mu\mu$, **520.9**$\mu\mu$), 512.0$\mu\mu$, 509.6$\mu\mu$, 482.1$\mu\mu$, 475.9$\mu\mu$, 469.5$\mu\mu$, 461.4$\mu\mu$, 444.3$\mu\mu$, 434.1$\mu\mu$, **427.7**$\mu\mu$, 417.3$\mu\mu$.

SAMARIUM, Sa. At. Wt. 150.4

Samarium is the least basic member of the cerite earth group and is somewhat similar to terbium of the yttrium earth group. Its salts are colored topaz yellow and are of the trivalent metal type. Its reactions are similar to those of the other members of the group. The double nitrate, according to the general rule given on p. 519, is the most soluble and least stable of the group.

TANTALUM, Ta, At. Wt. 181.5, and NIOBIUM, Nb, At. Wt. 93.1 *

These two rare elements, belonging to the nitrogen-vanadium group, form oxides of the formula R_2O_5, which behave as acid anhydrides and should have been considered, perhaps, under the acids. Since, however, tantalic and niobic acids are soluble, under certain conditions, in strong acids and from these solutions are precipitated by ammonia and ammonium sulphide, it seems better to consider them at this place.

Occurrence. — In the form of meta-acids these elements appear in the isomorphous minerals tantalite, $Fe(TaO_3)_2$, and niobite or columbite, $Fe(NbO_3)_2$, which are ferrous salts of tantalic and niobic acids. In tantalite a part of the tantalic acid is replaced by niobic acid and a part of the iron by manganese. Niobite shows an analogous behavior.

In the form of pyro acids the two elements occur as an isomorphous mixture $Y_4(Ta_2O_7)_3$ and $Y_4(Nb_2O_7)_3$, in the mineral yttrotantalite. Finally tantalum, and to some extent niobium, replaces the phosphorus in monazite, $(Ce,La,Di)PO_4$. Tin is usually found in all the above minerals and often tungsten; conversely cassiterite and wolframite often contain small quantities of niobic and tantalic acids.

Tantalite and niobite are attacked by fusing with potassium acid sulfate; impure niobic and tantalic acids are left undissolved upon treating the melt with water. Sulfuric acid can be removed from the residue only by heating with ammonium carbonate.

TANTALUM, Ta. At. Wt. 181.5 M. Pt. = 2850°. Sp. Gr. = 16.5

Metallic tantalum † is ductile, although the presence of a little impurity makes it harder than tool steel. On ignition in the air it assumes a yellow to blue tinge caused by a thin coating of oxide. Tantalum is not attacked by boiling H_2SO_4, HCl, HNO_3, or even aqua regia, but it is slowly dissolved by hydrofluoric acid with evolution of hydrogen; any metal remaining undissolved is then brittle on account of adsorbed hydrogen. The concentrated solution in hydrofluoric acid forms with concentrated KOH insoluble, crystalline potassium tantalum fluoride, K_2TaF_7. By evaporating the solution in

* Also called Columbium, Cb.

† W. VON BOLTON, *Z. Electrochemie*, **11**, 45 (1905).

HF with concentrated H_2SO_4 until the former acid is all expelled, the residue dissolves in a little cold water, but the solution becomes turbid on dilution or especially by boiling.

Tantalum forms two oxides, Ta_2O_4 and Ta_2O_5, the former being indifferent chemically and the latter is somewhat amphoteric but is usually regarded as the anhydride of a weak acid. After ignition, the pentoxide is insoluble in acids, except hydrofluoric acid and a mixture of sulfuric and hydrofluoric acids, it can be volatilized by heating with ammonium fluoride. Fusion of the oxide with caustic alkali in a silver crucible gives rise to alkali tantalates, both the meta- and hexatantalates being known; only the former are soluble in water.

Potassium hexatantalate, $K_8Ta_6O_{19} + 16\ H_2O$, is soluble in water and caustic potash solution; the corresponding sodium salt is soluble in water but not in caustic soda solution. If potassium hexatantalate is treated with hot water, a part of it goes into solution and undergoes hydrolysis, forming a colloidal solution of $H_8Ta_6O_{19}$. If CO_2 is conducted into the solution, the tantalic acid is completely precipitated in a flocculent condition. (Difference from niobic acid.) The remaining tantalates are all insoluble.

Tantalum pentachloride, $TaCl_5$, is formed by heating metallic tantalum, or a mixture of tantalum oxide and carbon, with dry chlorine; or, better, by heating with dry carbon tetrachloride. It melts at 211° and sublimes into a crystalline mass which is decomposed by water forming insoluble metatantalic acid. The pentachloride dissolves in sulfuric and in hydrochloric acids and is somewhat soluble in potassium hydroxide solution.

Tantalum fluoride is formed by dissolving tantalum pentoxide in hydrofluoric acid. (See below.)

Reactions in the Wet Way

A solution of potassium hexatantalate should be used.

1. **Mineral Acids.** — (*a*) **H_2SO_4** precipitates tantalic acid from cold, dilute solutions, and the precipitation becomes nearly quantitative on boiling. Hot, concentrated H_2SO_4 dissolves the precipitate produced by the dilute acid. On diluting the solution with water after it has become cold, the tantalic acid is reprecipitated (difference from niobium).

(*b*) **HCl** added to a concentrated solution at first produces a precipitate, which dissolves in an excess of the acid, forming an opalescent solution. From this solution sulfuric acid precipitates tantalic acid in the cold, but the precipitation is not quantitative even on boiling.

(*c*) **HNO_3** has the same action as HCl.

2. **NH_4OH** and **$(NH_4)_2S$** precipitate from the hydrochloric acid solutions either tantalic acid itself or an acid ammonium tantalate; tartaric acid prevents the precipitation.

3. **Na_2CO_3** produces a partial precipitation of tantalic acid when added to an acid solution of a tantalate, but the precipitate dissolves in an excess of the precipitant.

4. **H_2S** precipitates tantalic acid in the cold, especially from sulfuric acid solution, and the precipitate is almost quantitative.

5. **H_2O_2** dissolves freshly precipitated tantalic acid if acid or alkali is present. From the solution thus obtained, the tantalic acid is not precipitated by the above reagents unless the pertantalate is decomposed by boiling the alkaline solution or by the action of sulfurous acid.

6. **$K_3[Fe(CN)_6]$** and **KCNS** produce white precipitates.

7. **Tincture of Nutgalls** produces no precipitate (difference from niobic acid).

8. **$K_4[Fe(CN)_6]$** produces in acid solutions a light-yellow precipitate, which becomes brown on the addition of a little ammonia.

9. **$H[KF_2]$**. — If a concentrated solution of tantalic acid in hydrofluoric acid is treated with KF, the difficultly soluble $K_2[TaF_7]$ is formed, which separates from the solution in the form of orthorhombic needles (200 parts of water dissolve 1 part of salt) (difference from niobium). On boiling the solution of potassium tantalic fluoride, the very difficultly soluble oxyfluoride precipitates ($K_4Ta_4O_5F_{14}$). By means of this reaction the merest trace of tantalic acid can be detected in the presence of niobic acid.

10. **Zn** and **HCl** do not produce colored solutions (difference from niobium).

Reactions in the Dry Way

Ta_2O_5 is infusible. The salt of phosphorus bead remains colorless in both oxidizing and reducing flames. The addition of $FeSO_4$ does not cause the formation of a blood-red color. (Difference from Ti and Nb.)

NIOBIUM. At. Wt. 93.1. Sp. Gr. = 12.7. M. Pt. = 1950° C.*

The metal niobium, also called columbium, is very similar to tantalum but is more readily attacked by acids.

Niobium forms three oxides: Nb_2O_2, Nb_2O_4, and Nb_2O_5, of which the last is an acid anhydride. Nb_2O_5, like Ta_2O_5, is insoluble in acids after it has been ignited and is not rendered soluble by fusing with

* WERNER VON BOLTON, *Chem. Zentralbl.*, **1905**, I, 586.

potassium pyrosulfate. The melt dissolves in cold water, but niobic acid separates from the solution on boiling. By fusing with KOH or K_2CO_3, potassium hexaniobate, $K_8Nb_6O_{19} \cdot 16\,H_2O$, is formed, which is soluble in water. The corresponding sodium salt is insoluble in caustic soda solution, but soluble in water (1 : 200 at 15° and 1 : 75 at 100°). It is more than twice as soluble as the corresponding tantalate.

Sodium hexaniobate is largely hydrolyzed in aqueous solution, forming a colloidal solution of niobic acid, $H_8Nb_6O_{19}$. By passing CO_2 through this solution for half an hour, there is no precipitation of niobic acid, but only after long standing. (Difference from tantalic acid.)

Reactions in the Wet Way

Use a solution of potassium hexaniobate.

1. **Mineral Acids** produce in alkali niobate solutions a white, amorphous precipitate of niobic acid, which is only slightly soluble in an excess of the acid. Concentrated sulfuric acid, however, dissolves the niobic acid on warming, and the solution remains clear after being diluted with cold water. (Difference from tantalum.)

By boiling the diluted solution, the niobic acid is precipitated almost completely, but in a very finely divided condition, such that it is hard to filter. If the acid is exactly neutralized with ammonia, the niobic acid is precipitated in a flocculent condition easy to filter. It is best to wash such a precipitate with 0.5 per cent ammonia water or with 1 per cent acetic acid. Washing with pure water causes a turbid filtrate and mineral acids should not be used.

If a solution of niobic acid in sulfuric acid is poured into a concentrated solution of ammonium sulfate, no niobic acid is precipitated by boiling. (Difference from tantalic acid.)

If the niobic acid is treated with boiling hydrochloric acid, it dissolves only slightly, but on pouring off the acid, the residue is soluble in water.*

Carbonic acid decomposes sodium niobate to some extent. On the other hand, a niobate solution prepared after fusing with sodium carbonate and potassium nitrate is not decomposed by CO_2. (Difference from tantalic acid.)

2. **NH_4OH** and **$(NH_4)_2S$** precipitate niobic acid from the sulphuric acid solution, and the precipitate is soluble in HF.

3. **H_2O_2** reacts as with a tantalate.

* This behavior reminds one of metastannic acid. (Cf. p. 273.)

4. **Tincture of Nutgalls** produces no precipitate.

5. $K_4[Fe(CN)_6]$ produces a grayish-green precipitate.

6. $H[KF_2]$. — If niobic acid is dissolved in an excess of HF and KF is then added, readily soluble potassium niobic fluoride is formed (12.5 parts of water dissolve 1 part of the salt). By boiling the dilute aqueous solution, soluble potassium niobic oxyfluoride is formed, which is even more soluble. (Difference from tantalum.)

7. **Zinc** produces in an acid solution of a niobate a dirty-blue coloration which disappears after some time. (Difference from tantalum.)

Reactions in the Dry Way

The salt of phosphorus bead is blue, violet, or brown in the reducing flame (according to the amount of niobic acid which is present); the bead becomes red on the addition of $FeSO_4$.

Separation of Tantalum from Niobium *

Fuse the two oxides with a little sodium carbonate in a platinum crucible, cool, extract with hot water and filter off the undissolved sodium hexatantalate. Wash the residue with a solution of $NaHCO_3$ and conduct CO_2 into the filtrate, whereby some flocculent tantalic acid will be precipitated, but the niobic acid will remain in solution. Filter, unite this precipitate with the residue from the sodium carbonate fusion and dissolve both in sulfuric acid and hydrogen peroxide. Pass SO_2 into this solution and boil; tantalic acid will be precipitated. Similarly saturate the sodium carbonate solution of sodium niobate with SO_2 and niobic acid will be precipitated by boiling.

* Weiss-Landecker, *Z. anorg. Chem.*, **64**, 65–103 (1909), and Hauser-Lewite, *Z. angew. Chem.*, **1912**, 100.

METALS OF THE H_2S GROUP

THALLIUM, VANADIUM, MOLYBDENUM, TUNGSTEN, SELENIUM, TELLURIUM, RHODIUM, PALLADIUM, OSMIUM, IRIDIUM, RUTHENIUM

THALLIUM, Tl. At. Wt. 204.0. Sp. Gr. = 11.9. M. Pt. = 302°

Occurrence. — Thallium is found in nature very sparingly; in small amount in many varieties of pyrite, and accompanying potassium in carnalite and sylvite, in many lithium micas and in many mineral waters. It replaces the silver to a considerable extent in copper-silver selenide, in crookesite, $(AgTlCu)_2Se$, and in berzelianite, $(CuAgTl)_2Se$. There are no characteristic thallium minerals. The principal source of thallium is the dust from sulfuric acid plants where pyrite containing thallium is used.

Metallic thallium reminds one of lead in its color, softness, high specific gravity, and low melting-point. On bending, it *cries* like tin.

Thallium dissolves readily in nitric and sulfuric acids, but not so readily in hydrochloric acid. It forms two oxides: thallous oxide, Tl_2O, and thallic oxide, Tl_2O_3; both are anhydrides of bases and from them thallous and thallic salts are derived.

Reactions in the Wet Way

A. Thallous Compounds

Thallous compounds are colorless and soluble in water as a rule. The sulfide, chloride, bromide, iodide, and chromate are insoluble in water. Thallous oxide is a dark powder; its aqueous solution reacts alkaline and absorbs carbon dioxide with avidity. Boiling with nitric acid does not oxidize thallous salts but aqua regia causes the formation of trivalent thallic salt.

Thallium is like lead in respect to its specific gravity and to the solubility of its halogen compounds; but, on the other hand, it is similar to the alkalies with regard to the solubility and alkaline reaction of the hydroxide and carbonate, and with regard to its forming an insoluble chloroplatinate, an alum and an insoluble cobaltinitrite.

Use a solution of thallous sulfate for the following reactions:

1. H_2S causes no precipitation from solutions which contain mineral acids; in neutral solutions, thallium is incompletely precipitated as black thallous sulfide, Tl_2S. Tl_2S is readily soluble in mineral acids, but insoluble in acetic acid and alkaline sulfides. It is oxidized readily on standing in the air to thallous sulfate.

2. **$(NH_4)_2S$** precipitates all of the thallium as Tl_2S.

3. **KOH, NaOH,** or **NH_4OH** produces no precipitation.

4. **Alkali Carbonates** cause precipitation only in very concentrated solutions, for thallous carbonate is fairly soluble (100 parts of water dissolve 5 parts of the salt).

5. **HCl** produces a heavy, white precipitate of thallous chloride, very slightly soluble in water, and still less so in water containing a little hydrochloric acid.

6. **KI** precipitates yellow thallous iodide, TlI, from even the most dilute solutions; this is the most sensitive reaction for thallium. Unlike lead iodide, it dissolves in cold sodium thiosulfate solution.

7. **Alkali Chromates** precipitate yellow thallous chromate, insoluble in cold nitric or sulfuric acid.

8. **$H_2[PtCl_6]$** precipitates light-yellow thallium chloroplatinate, which is quite insoluble in water; 1 part dissolves in 15,600 parts of water at 15° C. and in 1950 parts of water at 100° C.

9. **$Al_2(SO_4)_3$.** — If a solution of thallous sulfate is treated with aluminium sulfate and the solution is then allowed to crystallize, glistening, colorless octahedrons are obtained of thallium alum, $TlAl(SO_4)_2 + 12\ H_2O$.

10. **$K_3[Fe(CN)_6]$** precipitates brown $Tl(OH)_3$ in alkaline solutions:

$$2\ [Fe(CN)_6]^{---} + 3\ OH^- + Tl^+ \rightarrow 2\ [Fe(CN)_6]^{--} + Tl(OH)_3.$$

11. **Zinc, Aluminium** or **Magnesium** precipitates metallic thallium in the form of black, tiny crystals:

$$Zn + 2\ Tl^+ \rightarrow Zn^{++} + 2\ Tl.$$

12. **Sodium Cobaltinitrite** precipitates light-red thallous cobaltinitrite:

$$[Co(NO_2)_6]^{---} + 3\ Tl^+ \rightarrow Tl_3[Co(NO_2)_6].$$

B. Thallic Compounds

Thallic compounds cannot as a rule be prepared by the oxidation of thallous compounds (with the exception of thallic chloride, which is readily obtained by the action of chlorine water upon thallous chloride). They are obtained by the solution of thallic oxide * in acids, and can be distinguished from thallous compounds by the ease with which they suffer decomposition in aqueous solution. Thus thallic sulfate is decomposed on boiling its aqueous solution into thallic hydroxide and sulfuric acid; the nitrate behaves similarly.

The chloride, $TlCl_3$, is a hygroscopic and not very stable substance; on being heated to 100° C. chlorine is evolved with the formation of thallous chloride.

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* Tl_2O_3 is not attacked in the cold by concentrated sulfuric acid, but is dissolved on warming. The hydrated oxide, TlO(OH), is much more soluble.

1. ***KOH, NaOH,*** *and* ***NH₄OH*** *precipitate brown thallic hydroxide,* $Tl(OH)_3$, *from solutions of thallic salts, which changes to* $TlO(OH)$ *on standing in the air; it is difficultly soluble in acids and insoluble in an excess of alkali.*

2. **HCl** and **alkali chromates** do not cause precipitation.

3. **KI** precipitates thallous iodide with deposition of iodine.

$$I_3^- + Tl^{+++} \rightarrow TlI + I_2.$$

4. H_2S in acid solutions causes reduction with precipitation of sulfur,

$$H_2S + Tl^{+++} \rightarrow Tl^+ + 2\,H^+ + S.$$

If the acid is neutralized, thallous sulfide precipitates.

Reactions in the Dry Way

Thallium salts color the non-luminous gas-flame a beautiful emerald green. The thallium spectrum consists of a green line at **535.0,** nearly coincident with the green barium line at 534.7.

INDIUM, IN. At. Wt. 114.8

Sp. Gr. 7.3. M. Pt. 155°

Indium was discovered in zinc ores and has also been found associated with tungsten. The free element is a white, lustrous metal resembling platinum in appearance. It is very soft and ductile and leaves a mark on paper. It is oxidized slowly in contact with air but less readily than zinc. The metal dissolves in dilute hydrochloric and sulfuric acids with liberation of hydrogen and formation of trivalent indium ions:

$$2\,In + 6\,H^+ \rightarrow 2\,In^{+++} + 3\,H_2\uparrow.$$

Nitric acid dissolves it readily but with sulfuric acid the anhydrous salt separates out.

Indium forms three chlorides, WCl, WCl_2 and WCl_3 but only the salts of the trivalent metal are stable in aqueous solutions. Indium oxide, In_2O_3, is pale yellow when cold and reddish brown when hot. Heating it in hydrogen gas or with carbon gives reduction to metal. The ignited oxide dissolves slowly in cold acids but more readily in hot, dilute acids. Indium salts are colorless; the sulfate, nitrate and chloride dissolve in water.

Reactions in the Wet Way

1. **KOH, NaOH** and **NH_4OH** precipitate white, gelatinous indium hydroxide:

$$In^{+++} + 3\,OH^- \rightarrow In(OH)_3.$$

The precipitate resembles aluminium hydroxide in appearance and behavior. Tartaric acid prevents its formation. It dissolves in excess of sodium or potassium hydroxide solution but the liquid becomes turbid on standing and boiling with ammonium chloride causes the reprecipitation of the hydroxide.

2. **Na_2CO_3, K_2CO_3** and **$(NH_4)_2CO_3$** precipitate white, gelatinous $In_2(CO_3)_3$. It dissolves in an excess of cold ammonium carbonate solution but reprecipitates on boiling.

3. **$BaCO_3$** precipitates a basic salt even in the cold (difference from Zn, Mn, Co, Ni and Fe).

4. **Na_2HPO_4** gives a white, voluminous precipitate.

5. **$(NH_4)_2C_2O_4$** precipitates white, crystalline indium oxalate from concentrated solutions.

6. **$NaC_2H_3O_2$** added to a boiling, nearly-neutral solution of indium sulfate causes the precipitation of basic indium sulfate.

7. **H_2S** in neutral or acetic acid solutions gives a yellow precipitate of indium sulfide:

$$2\,In^{+++} + 3\,H_2S \rightarrow In_2S_3 + 6\,H^+.$$

The precipitate is not formed, except on dilution, if the solution contains considerable mineral acid.

8. **$(NH_4)_2S$** gives a white sulfide precipitate. By boiling the yellow sulfide with yellow ammonium sulfide, it is changed to white sulfide and dissolves to some extent; on cooling, a white voluminous sulfide precipitate is formed. It is not quite clear just what symbols should be assigned to the white and yellow sulfide precipitates.

9. **$K_4[Fe(CN)_6]$** gives a white precipitate of indium ferrocyanide.

10. **$K_3[Fe(CN)_6]$**, **KCNS** and **$K_2Cr_2O_7$** give no precipitation. **K_2CrO_4** produces a yellow precipitate.

11. **Zinc** precipitates indium as white, lustrous flakes.

Reactions in the Dry Way

Heated on charcoal, the surface of the charcoal is given a lustrous metallic coating. Indium salts color the flame a peculiar bluish violet. In the spectrum two distinct blue lines are seen at 451.1$\mu\mu$ and 410.1$\mu\mu$.

GALLIUM, Ga. At. Wt. 70.1

Sp. Gr. = 5.96. M. Pt. = 30.1°

Gallium is of quite common occurrence in small quantities. It is found in many samples of sphalerite and in bauxites as well as in other minerals. It is a hard, white metal which is not very ductile and is not easily oxidized.

Hydrochloric acid, potassium hydroxide and ammonia dissolve gallium with evolution of hydrogen gas.

$$Ga + 2\,H^+ \rightarrow Ga^{++} + H_2\uparrow,$$

$$Ga + 2\,OH^- \rightarrow [GaO_2]^{--} + H_2\uparrow,$$

$$Ga + 2\,H_2O^- + 4\,NH_3 \rightarrow [Ga(NH_3)_4]^{++} + H_2\uparrow + 2\,OH^-.$$

The metal is passive to cold nitric acid but on heating it dissolves and red vapors are evolved.

$$Ga + 6\,HNO_3 \rightarrow Ga(NO_3)_3 + 3\,H_2O + 3\,NO_2\uparrow.$$

Gallium forms bivalent gallous salts and trivalent gallic salts. The gallous compounds are unstable and easily oxidized. Gallic oxide, Ga_2O_3, and its hydroxide, $Ga(OH)_3$, are white. Gallic salts are colorless or white. Gallic chloride is a colorless, hygroscopic substance which melts at 75° and boils at 215–220°. Evaporation of gallic chloride solutions causes volatilization of gallic chloride but there is no loss of gallium if sulfuric acid is present.

Reactions of Gallic Salts in the Wet Way

1. **NaOH, KOH** and **NH_4OH** precipitate white, flocculent gallic hydroxide:

$$Ga^{+++} + 3\,OH^- \rightarrow \mathbf{Ga(OH)_3},$$

readily soluble in an excess of precipitant:

$$\mathbf{Ga(OH)_3} + 3\,OH^- \rightarrow [GaO_3]^{---} + 3\,H_2O.$$

Boiling the ammoniacal solution causes slow reprecipitation of the hydroxide. Tartaric acid prevents precipitation by ammonia.

2. **Na_2CO_3** and **$(NH_4)_2CO_3$** give white precipitates. Excess of ammonium carbonate causes the precipitate to redissolve.

3. **$BaCO_3$** causes complete precipitation in the cold.

4. **H_2S** gives no precipitate in acid solutions (even acetic or tartaric acid) provided no other precipitable ion is present. White gallium sulfide, however, is precipitated with sulfides of zinc, silver, copper, iron and arsenic.

5. **Ammonium Sulfide** gives a precipitate only when another insoluble sulfide is also formed.

6. **Ammonium Acetate** causes the formation of an insoluble basic acetate from boiling dilute solutions containing not too much of the precipitant.

7. **$Cu(OH)_2$** and **MnS** cause precipitation of gallic hydroxide. With the manganous sulfide, hydrogen sulfide is evolved. By means of cupric hydroxide, gallium ions can be separated from ions of lead, cobalt, nickel, iron, thallium, beryllium and the rare earths.

Reactions in the Dry Way

Gallium compounds give two violet lines in the spark spectrum between the G and H lines at 417.0 and 403$\mu\mu$. With the Bunsen flame only one faint line is seen.

VANADIUM, V. At. Wt. 51.0. Sp. Gr. = 5.8. M. Pt. = 1730°

Occurrence. — Vanadinite, $Pb_5(VO_4)_3Cl$; carnotite;* mottramite, $(Cu,Pb)_5V_2O_{10} + 2\,H_2O$; many clays and in almost all granite.

Metallic vanadium is silver white or pale gray. It is often obtained from its ores in the form of ferro-vanadium which is used in steel making. Vanadium is found in various metallurgical products and sometimes in caustic soda. The metal has strong reducing power and is soluble in hydrochloric acid.

Vanadium, like nitrogen, forms five oxides: V_2O, V_2O_2, V_2O_3, V_2O_4, V_2O_5.

The first three of these oxides are basic anhydrides. Compounds representing these valencies of vanadium are not encountered in qualitative analysis except, to some extent, in the tests for vanadium with strong reducing agents. Vanadous oxide, V_2O_2, is dark gray and lustrous. It is insoluble in water but dissolves in dilute acids to form blue solutions which, because of their strong reducing powers, decolorize organic dyestuffs.

Vanadic oxide, V_2O_3, is black, insoluble in acids (except hydrofluoric and nitric acids) and in alkali hydroxide solutions. By ignition in hydrogen, it is not reduced but on standing in the air it slowly changes into vanadyl oxide V_2O_4. Acid solutions containing trivalent vanadic salts are green. The oxides V_2O_4 and V_2O_5 represent the types of vanadium compounds usually encountered in analytical chemistry.

Vanadyl oxide, V_2O_4 (also called vanadium tetroxide), is the anhydride of hypovanadic acid, $V_2O_2(OH)_4$. This compound is an amphoteric substance and forms salts with both acids and bases. V_2O_4 itself is a blue powder, soluble in concentrated acids, forming blue divanadyl salts:

$$V_2O_4 + 2\,H_2SO_4 = V_2O_2(SO_4)_2 + 2\,H_2O.$$

If the solution of divanadyl sulfate is treated with sodium carbonate or ammonia (avoiding excess), hypovanadic acid separates out as a grayish-white precipitate, which, like the anhydride, is soluble in acids with blue color and in alkalies with a brown color. The alkali hypovanadates correspond to the symbols $Na_2V_2O_5$ and $Na_2V_4O_9$. Hypovanadates of other metals are for the most part insoluble in water and such precipitates may form when an acid solution containing vanadium is neutralized. The divanadyl compounds are readily formed by

* According to FRIEDEL and CUMENGE, carnotite contains 18 per cent V_2O_5 and 55 per cent VO_2, as well as K, Ca, Ba, H, As, and P. (Cf. HILLEBRAND and RANSOME, *Am. J. Science*, **10**, 138.)

reducing solutions of the pentoxide in mineral acids with sulfurous acid (cf. p. 544), and serve, on account of their blue color, for the detection of vanadium. By heating with nitric acid or aqua regia, as well as by fusion with an alkaline oxidizing flux, all the lower oxides are changed into vanadium pentoxide, V_2O_5, or one of its salts.

Vanadium pentoxide, V_2O_5, is the anhydride of vanadic acid and is an orange-red, crystalline mass, which is readily fusible but non-volatile. It is only slightly soluble in water, forming a faintly-acid, yellow solution, but readily soluble in concentrated solutions of caustic alkalies, forming vanadates.

Like phosphoric acid, vanadic acid exists in the form of meta-, pyro-, ortho-, and poly-compounds, of which the meta-compounds are the most stable and the ortho-compounds the least so. Thus an aqueous solution of potassium or sodium orthovanadate is hydrolyzed, even in the cold, into the pyro-salt and alkali hydroxide,

$$2\,Na_3VO_4 + H_2O \rightleftarrows Na_4V_2O_7 + 2\,NaOH,$$

and on boiling the meta-salt is formed:

$$Na_4V_2O_7 + H_2O \rightleftarrows 2\,NaVO_3 + 2\,NaOH.$$

The meta-, pyro-, and ortho-salts of the alkalies are colorless or slightly yellow, while the polyvanadates, e.g., the tetra- and hexa-vanadates, are intensely orange or reddish. Thus the colorless or light-yellow solutions of the ortho-, meta-, and pyrovanadates are colored intensely orange on the addition of acid.

Strong acids dissolve vanadium pentoxide forming red or yellow solutions. Such solutions probably contain the quinquevalent vanadium in the cation as VO_2^+, VO^{+++} and possibly a little V^{+++++}. The equilibria between the vanadium in cations and in anions are illustrated by the following equations:

$$V_2O_7^{--} + 6\,H^+ \rightleftarrows 2\,VO_2^+ + 3\,H_2O,$$
$$2\,VO_2^+ + 6\,OH^- \rightleftarrows V_2O_7^{--} + 3\,H_2O,$$
$$V_2O_7^{--} + 10\,H^+ \rightleftarrows 2\,VO^{+++} + 5\,H_2O,$$
$$V_2O_7^{--} + 14\,H^+ \rightleftarrows 2\,V^{+++++} + 7\,H_2O,$$
$$2\,V^{+++++} + 14\,OH^- \rightleftarrows V_2O_7^{--} + 7\,H_2O.$$

In acid solutions, the vanadium is easily reduced to green vanadyl salt and the change takes place slowly on standing or by evaporating the solution in hydrochloric acid.

Besides the above types of vanadium compounds, this element exists as pervanadic acid, HVO_4, formed by the addition of hydrogen peroxide to the acid solution of a vanadate.

The reactions of quadrivalent and quinquevalent vanadium will be considered together; the other compounds are not common enough to make it necessary to describe their characteristic reactions.

Reactions in the Wet Way

1. **NH_4Cl.** — If a piece of solid ammonium chloride is added to a solution of an alkali vanadate, colorless ammonium metavanadate separates out,

$$Na_4V_2O_7 + 4\,NH_4Cl = 2\,NH_4VO_3 + 2\,NH_3 + H_2O + 4\,NaCl,$$

difficultly soluble in a concentrated solution of ammonium chloride.

2. **$Pb(C_2H_3O_2)_2$** precipitates vanadic acid quantitatively as yellow lead vanadate:

$$3\,Pb^{++} + 2\,VO_4^{---} \rightarrow Pb_3(VO_4)_2.$$

This precipitate, however, is more soluble in dilute nitric acid than is lead chromate, and it is possible to separate chromic acid from vanadic acid by treating the solution of the two acids with lead nitrate in dilute nitric acid solution; under the proper conditions all but a fraction of a milligram of the chromium is precipitated and 100 mgms. of vanadium yield no precipitate.* The vanadium can be detected in the filtrate by the H_2O_2 test.

3. **NH_4OH** added to a cold, green, acid solution of a vanadate, containing some vanadium in the form of cations, causes the color to become yellow. After the solution has been neutralized, no further change is produced if the solution contains none but alkali cations. In the presence of other cations, however, the vanadate ion acid behaves like phosphate ion toward ammonia; vanadates of ferric iron, aluminium, uranium and barium are likely to be precipitated by ammonia.

NH_4OH added to a solution of a vanadyl salt precipitates dark-gray hypovanadic acid:

$$V_2O_2Cl_4 + 4\,NH_4OH = 4\,NH_4Cl + V_2O_2(OH)_4.$$

The precipitation is not quantitative and small quantities of vanadium may remain in solution when the vanadyl salt is alone present. If, however, an excess of ferric chloride is added to the solution, the vanadium is quantitatively precipitated upon the addition of ammonia. This is true both of vanadic acid and of vanadyl salt, ferric vanadate and ferric hypovanadate being precipitated with the ferric hydroxide. Instead of ferric chloride, an aluminium or uranium salt may be used for the same purpose.

Sodium Hydroxide added to an acid solution of quinquevalent vanadium gives a brown precipitate soluble in an excess of the base and giving a yellowish-green solution.

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* The solution is neutralized exactly with NaOH, 2 cc. of HNO_3 (sp. gr. 1.20) are added together with an excess of 20 per cent $Pb(NO_3)_2$ solution.

4. $(NH_4)_2S$ produces no precipitation, but causes the solution to turn brown, owing to the formation of thio-salts.

If hydrogen sulfide is conducted into a strongly ammoniacal solution of a vanadate or hypovanadate, the solution at first turns yellowish-red, but the color slowly deepens until eventually a characteristic, brilliant, violet-red color is obtained when the solution has become saturated with H_2S. Ammonium salts interfere somewhat with this test, but their influence is overcome by the addition of a large excess of ammonia. The red color is probably caused by the formation of ammonium thiovanadate. As little as 0.2 mgm. of vanadium can be recognized by the red color.

The addition of acid to the red solution produces a black precipitate of V_2S_4 or V_2S_5. The precipitation is not quantitative; the filtrate is always colored blue and contains detectable amounts of vanadyl salts. The precipitate is soluble in alkalies, alkali carbonates, and in alkali sulfides, forming a brown solution.

Molybdenum gives a similar red color, in case it was not completely removed by previous treatment with hydrogen sulfide in acid solution, and obscures the above test or may be mistaken for vanadium.

Ammonium sulfide added to an acid solution of quinquevalent vanadium, precipitates brown V_2S_5, slowly dissolved by an excess of the reagent.

5. H_2S gives no precipitation in acid solution, but reduces compounds of vanadic acid to divanadyl compounds, so that the solution is colored blue:

$$2\,H_3VO_4 + H_2S + 4\,HCl = V_2O_2Cl_4 + 6\,H_2O + S.$$

6. **Reducing Agents** (SO_2, H_2S, HBr, alcohol, oxalic and tartaric acids, sugar, etc.) reduce acid solutions containing vanadates to blue, vanadyl salts:

$$2\,VO_4^{---} + SO_3^{--} + 10\,H^+ \rightarrow [V_2O_2]^{++++} + SO_4^{--} + 5\,H_2O.$$

HI reduces vanadic acid to green salt of V_2O_3:

$$VO_4^{---} + 2\,I^- + 8\,H^+ \rightarrow V^{+++} + I_2 + 4\,H_2O.$$

The green color only appears after the iodine has been removed by continued boiling of the solution.

Metals, such as Zn, Al, and Cd, cause still further reduction of vanadic acid, so that the solution turns at first blue (vanadyl salt), then green (trivalent vanadium) and finally violet or lavender blue (bivalent vanadium). Ammonium hydroxide added to the fully reduced solution gives a brown precipitate which oxidizes easily.

Boiling an acid solution of a vanadate with concentrated hydrochloric acid and alcohol reduces the vanadium quantitatively to divanadyl salt. Treatment of vanadic acid with ferrous salt also reduces the former to divanadyl salt and the excess of the ferrous iron can be oxidized by cold potassium dichromate solution without oxidizing the vanadium.

7. H_2O_2. — If an acid solution of a vanadate is treated with a few drops of H_2O_2 and shaken, the solution becomes colored reddish brown owing to the formation of pervanadic acid, HVO_4, insoluble in ether. This is a very delicate reaction.

8. **Mercurous Nitrate** precipitates white mercurous vanadate from neutral solutions of a vanadate; the precipitate is soluble in nitric acid.

9. **Oxidizing Agents** convert divanadyl compounds into vanadic acid. The oxidation may be effected by bromine in hydrochloric acid solution,

$$[V_2O_2]^{++++} + Br_2 + 6\,H_2O \rightarrow 2\,VO_4^{---} + 2\,Br^- + 12\,H^+,$$

by dilute potassium permanganate in hot, very dilute sulfuric acid solution,

$$5\,[V_2O_2]^{++++} + 2\,MnO_4^- + 22\,H_2O \rightarrow 10\,VO_4^{---} + 2\,Mn^{++} + 44\,H^+,$$

or by sodium peroxide in alkaline solution:

$$[V_2O_2]^{++++} + Na_2O_2 + 8\,OH^- \rightarrow 2\,VO_4^{---} + 2\,Na^+ + 4\,H_2O.$$

Chromium, aluminium, vanadium and uranium may be separated from iron, nickel, cobalt and manganese by means of this reaction; the chromate is left in solution as sodium chromate, Na_2CrO_4, the aluminium as sodium aluminate, $NaAlO_2$, the vanadium as sodium vanadate, Na_3VO_4, the uranium as sodium peruranate, and the zinc as sodium zincate, Na_2ZnO_2; while the iron is precipitated as $Fe(OH)_3$, the nickel as $Ni(OH)_2$, the cobalt as $Co(OH)_3$, and the manganese as hydrated MnO_2.

10. **Potassium Ferrocyanide** added to an acid solution of quinquevalent vanadium gives a green, flocculent precipitate of vanadium ferrocyanide.

11. **Barium Chloride,** but not strontium and calcium chloride, **silver nitrate** and **lead acetate** give yellow precipitates which become white on standing or on heating.

12. To distinguish between ortho and meta vanadates, the following reactions serve:

Copper salts give a bluish-green, pulverulent precipitate with meta vanadates and an apple-green precipitate with ortho vanadates. Lead salts give a white precipitate with ortho vanadates and silver salts give an orange-red precipitate with ortho vanadates.

13. **Uranyl Salts** added to an ammoniacal, or slightly acid, solution containing ammonium acetate give a precipitate of uranyl ammonium vanadate $(UO_2)NH_4VO_4 \cdot H_2O$. By means of this reaction vanadate ions can be separated from alkali, alkaline earth, manganese, zinc and copper ions.

Detection of Vanadium in Rocks (Hillebrand) *

Fuse 5 gms. of the finely powdered rock with 20 gms. of Na_2CO_3 and 3 gms. of $NaNO_3$. Cool, extract the fused mass with water, reduce any green manganate by the addition of a little alcohol, and filter the solution which contains the sodium salts of arsenic, phosphoric, molybdic, chromic, vanadic and tungstic acids. Nearly

* *Amer. J. Science*, **1898**, p. 209.

4. $(NH_4)_2S$ produces no precipitation, but causes the solution to turn brown, owing to the formation of thio-salts.

If hydrogen sulfide is conducted into a strongly ammoniacal solution of a vanadate or hypovanadate, the solution at first turns yellowish-red, but the color slowly deepens until eventually a characteristic, brilliant, violet-red color is obtained when the solution has become saturated with H_2S. Ammonium salts interfere somewhat with this test, but their influence is overcome by the addition of a large excess of ammonia. The red color is probably caused by the formation of ammonium thiovanadate. As little as 0.2 mgm. of vanadium can be recognized by the red color.

The addition of acid to the red solution produces a black precipitate of V_2S_4 or V_2S_5. The precipitation is not quantitative; the filtrate is always colored blue and contains detectable amounts of vanadyl salts. The precipitate is soluble in alkalies, alkali carbonates, and in alkali sulfides, forming a brown solution.

Molybdenum gives a similar red color, in case it was not completely removed by previous treatment with hydrogen sulfide in acid solution, and obscures the above test or may be mistaken for vanadium.

Ammonium sulfide added to an acid solution of quinquevalent vanadium, precipitates brown V_2S_5, slowly dissolved by an excess of the reagent.

5. H_2S gives no precipitation in acid solution, but reduces compounds of vanadic acid to divanadyl compounds, so that the solution is colored blue:

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6. **Reducing Agents** (SO_2, H_2S, HBr, alcohol, oxalic and tartaric acids, sugar, etc.) reduce acid solutions containing vanadates to blue, vanadyl salts:

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HI reduces vanadic acid to green salt of V_2O_3:

$$VO_4^{---} + 2\,I^- + 8\,H^+ \rightarrow V^{+++} + I_2 + 4\,H_2O.$$

The green color only appears after the iodine has been removed by continued boiling of the solution.

Metals, such as Zn, Al, and Cd, cause still further reduction of vanadic acid, so that the solution turns at first blue (vanadyl salt), then green (trivalent vanadium) and finally violet or lavender blue (bivalent vanadium). Ammonium hydroxide added to the fully reduced solution gives a brown precipitate which oxidizes easily.

Boiling an acid solution of a vanadate with concentrated hydrochloric acid and alcohol reduces the vanadium quantitatively to divanadyl salt. Treatment of vanadic acid with ferrous salt also reduces the former to divanadyl salt and the excess of the ferrous iron can be oxidized by cold potassium dichromate solution without oxidizing the vanadium.

7. H_2O_2. — If an acid solution of a vanadate is treated with a few drops of H_2O_2 and shaken, the solution becomes colored reddish brown owing to the formation of pervanadic acid, HVO_4, insoluble in ether. This is a very delicate reaction.

MOLYBDENUM, Mo. At. Wt. 96.0. M. Pt. = 2500°?

Occurrence. — Molybdenite, MoS_2; wulfenite, $PbMoO_4$; powellite, $CaMoO_4$. Metallic molybdenum is the color of tin, is hard and easily oxidized by heating in the air. As ferro-molybdenum it is used in the manufacture of alloy steels such as are used for high-speed tools. The metal dissolves in nitric acid, aqua regia and in concentrated sulfuric acid. Molybdenum has a valence of 2, 3, 4, and 6, and forms the following oxides: MoO, Mo_2O_3, MoO_2, and MoO_3. The first three are basic anhydrides, while the last oxide, MoO_3, is an acid anhydride, forming a white mass (yellow when warm) which is readily fusible, but very difficultly volatile. When heated strongly, colorless, transparent, thin, orthorhombic plates of MoO_3 may be obtained from the fumes. MoO_3 is only very slightly soluble in water, but dissolves readily in alkalies and in ammonia, forming molybdates. Molybdic acid itself can be obtained as a solid mass by acidifying the solution of an alkali molybdate; it is soluble in an excess of the acid (difference from tungstic acid). In the acid solutions, probably some hexavalent molybdenum cations are present. The most important commercial molybdate is the acid ammonium molybdate, corresponding to the formula:

$$(NH_4)_6Mo_7O_{24} + 4\,H_2O \quad \text{or} \quad 3\,(NH_4)_2MoO_4 \cdot 4\,MoO_3 \cdot 4\,H_2O.$$

Reactions in the Wet Way

A solution of ammonium molybdate should be used.

The alkali molybdates are soluble in water; the remaining salts are mostly insoluble in water but soluble in acids.

1. **Dilute Acids** precipitate from concentrated alkali molybdate solutions white H_2MoO_4, soluble in an excess of acid.

Concentrated Sulfuric Acid. — If a trace of a molybdenum compound is evaporated with a drop of concentrated sulfuric acid almost to dryness in a porcelain dish, the mass is colored intensely blue. This is an exceedingly delicate reaction.

Antimony pentoxide, considerable stannic oxide and other impurities interfere with this reaction.

2. **H_2S** at first colors acid molybdenum solutions blue, and precipitates, little by little, the molybdenum as brown molybdenum trisulfide, MoS_3, soluble in ammonium sulfide, forming a brown solution from which MoS_3 is reprecipitated by the addition of acids. Molybdenum sulfide is oxidized by treatment with concentrated nitric acid, or by roasting in the air, into MoO_3.

3. Zinc. — If a molybdate solution which is acid with hydrochlori or sulfuric acid is treated with zinc, the solution is colored at first blue then green, and finally brown. Other reducing agents such as $SnCl_2$ $Hg_2(NO_3)_2$, etc., cause the same reaction.

4. SO_2 does not reduce dilute, strongly acid solutions of molybdates either in the cold or on heating. Neutral or slightly acid solutions are reduced and colored blue.

5. **KCNS** causes no change when added to acid molybdenum solutions, but if the solution is then treated with zinc or stannous chloride, a blood-red coloration is produced on account of the formation of molybdenum thiocyanate; the reaction also takes place in the presence of phosphoric acid (difference from iron). If the solution is shaken with ether, the colored compound is dissolved in the latter.

Tartaric acid, owing to the formation of complex ions, tends to prevent this reaction.

6. **Sodium Phosphate.** — If a few drops of a solution of sodium phosphate are added to a molybdate solution strongly acid with nitric acid, a yellow crystalline precipitate of ammonium phosphomolybdate is formed, slowly in the cold, but much more quickly on warming the solution (cf. Phosphoric Acid, p. 404). Arsenic acid causes the precipitation of a similar compound (cf. p. 246).

7. **Mercurous Nitrate** precipitates yellow mercurous molybdate from neutral solutions; the precipitate is soluble in nitric acid.

8. **Lead Acetate** precipitates white lead molybdate, soluble in nitric acid.

9. **Potassium Ferrocyanide** produces a reddish brown precipitate. A very sensitive test.

Molybdenum solutions containing free oxalic, acetic or phosphoric acids usually give no precipitate with potassium ferrocyanide, but merely a brown coloration. Molybdenum ferrocyanide is insoluble in dilute mineral acids but is dissolved by concentrated hydrochloric acid and reprecipitated upon diluting. It is readily soluble in caustic alkali and ammonia solutions, in which respect it is different from the uranyl and cupric ferrocyanides (pp. 164 and 233). To detect the ferrocyanide ion in molybdenum ferrocyanide, dissolve the salt in ammonia, saturate the ammoniacal solution with H_2S, acidify with dilute H_2SO_4, filter off the MoS_3 and test the filtrate with ferric chloride solution (p. 159).

10. H_2O_2.—If a solution to be tested for molybdenum is evaporated to dryness on the water-bath, the residue treated with a little concentrated ammonia and then with hydrogen peroxide, the ammoniacal solution is immediately turned pink or red. Then, by evaporating to dryness again and treating the residue with sulfuric or nitric acid, yellow permolybdic acid, $HMoO_4$, is obtained.

11. $FeSO_4$ and sulfuric acid added to an acid solution of molybdate gives a permanent blue color.

Reactions in the Dry Way

Alkali molybdates, alone or with sodium carbonate, are reduced on charcoal to gray molybdenum, a white incrustation of MoO_3 being formed at the same time.

Salt of Phosphorus Bead. — All molybdenum compounds color the bead, but the color depends upon the concentration. In the oxidizing flame the hot bead is colored brownish-yellow to yellow; it becomes yellowish-green on cooling and finally colorless. In the reducing flame the bead becomes dark brown when hot and grass green when cold. The borax bead is similar but not quite as characteristic.

Separation of Molybdenum, Arsenic, Antimony, and Tin

These elements are all precipitated as sulfides upon the introduction of hydrogen sulfide into an acid solution. They are separated from the members of the copper group by treatment with ammonium polysulfide solution, in which their sulfides are soluble. On acidifying this solution of the thio-salts with dilute hydrochloric acid, the molybdenum, arsenic, antimony and tin are reprecipitated as sulfides.

Filter off this precipitate, wash, dry and introduce it, little by little, into a nickel crucible containing a molten mixture of 10 parts Na_2O_2, and 10 parts Na_2CO_3 for each part of sulfide precipitate. Fuse the contents of the crucible, after all the sulfide has been introduced, for ten minutes over the Bunsen burner, then cool and extract with cold water. The aqueous solution thus obtained may contain sodium arsenate and sodium molybdate and the insoluble residue may consist of sodium antimonate and tin dioxide. Filter off this residue and wash it with a normal solution of sodium hydroxide. Test the filtrate for arsenic by acidifying with hydrochloric acid, making strongly ammoniacal and adding magnesium mixture. A white, crystalline precipitate of magnesium ammonium arseniate is formed if arsenic is present, but only after standing for some time with a little arsenic. Saturate the filtrate from the magnesium ammonium arsenate precipitate, with hydrogen sulfide to convert any molybdenum present into ammonium thiomolybdate, and then acidify the solution with dilute hydrochloric acid. Filter off the precipitated sulfide, treat it with concentrated nitric acid in a porcelain crucible and test for molybdenum with concentrated sulfuric acid, as described on p. 547.

Test for Antimony and Tin. — Treat the residue insoluble in dilute caustic soda solution with a mixture of equal parts concentrated hydrochloric acid and water, place the solution in contact with a piece of platinum foil and test for antimony and tin as described on p. 292.

TUNGSTEN, W. At. Wt. 184. Sp. Gr. 19.1. M. Pt. = 3000°

Occurrence. — Tungsten is not very often found in nature, but there are a number of well-crystallizing tungsten minerals, such as the minerals of the Scheelite group.

Scheelite, $CaWO_4$; cuproscheelite, $(CaCu)WO_4$; reinite, $FeWO_4$; stolzite, $PbWO_4$. These minerals all crystallize in the tetragonal system and form with powellite, $CaMoO_4$, and wulfenite, $PbMoO_4$, a very

interesting isomorphous group. Another isomorphous group, which consists of minerals crystallizing in the monoclinic system, is formed by hübnerite, $MnWO_4$; wolframite, $(MnFe)WO_4$, and ferberite, $FeWO_4$. The most important tungsten mineral is wolframite, which is usually contaminated with small amounts of silicic, tantalic, and niobic acids. Tungsten forms two oxides, WO_2 and WO_3.

WO_2 is a brown powder, readily obtained by heating WO_3 to dull redness in a stream of hydrogen. It is pyrophoric and must, therefore, be cooled in a stream of hydrogen before it is allowed to come into contact with the air. By igniting strongly in a stream of hydrogen, metallic tungsten is obtained, which is stable in the air. This behavior is important and is taken advantage of in the quantitative determination of tungsten.

Tungsten is used in the form of thin metallic filaments in incandescent electric lamps. Ferro-tungsten is used for making self-hardening or alloy steels.

WO_3 is an acid anhydride obtained by the ignition of tungstic acid of ammonium or mercurous tungstates, or by the oxidation of the dioxide on heating in the air.

The trioxide is a canary-yellow powder, insoluble in water and dilute acids, and only slightly soluble in concentrated hydrochloric and hydrofluoric acids. It dissolves readily by warming with potassium or sodium hydroxides, and less readily in ammonia. It is most easily dissolved by fusing with sodium carbonate, sodium tungstate being formed:

$$WO_3 + Na_2CO_3 = Na_2WO_4 + CO_2\uparrow.$$

It is changed to potassium tungstate by fusing with potassium pyrosulfate:

$$WO_3 + K_2S_2O_7 = K_2WO_4 + 2\,SO_3\uparrow.$$

If the product of this last fusion is treated with water, usually none of the tungsten goes into solution, because if an excess of potassium pyrosulfate is present (which is usually the case) it reacts with the potassium tungstate, forming free tungstic acid:

$$K_2WO_4 + K_2S_2O_7 + H_2O = 2\,K_2SO_4 + H_2WO_4.$$

If not enough pyrosulfate remains to complete the above decomposition, some of the tungsten will be dissolved, but never all of it. If a little sulfuric acid is added to the water, none of the tungsten will go into solution. This property enables one to separate tungsten from titanium. If ammonium carbonate is added, all of the tungsten dissolves, which enables us to separate tungstic from silicic acid.

Reactions in the Wet Way

A solution of sodium tungstate should be used.

1. **Mineral Acids,** HCl, HNO_3, H_2SO_4, produce, in the cold, a white, amorphous precipitate of hydrated tungstic acid, $H_2WO_4 + H_2O$.* By boiling the solution, the yellow anhydrous acid H_2WO_4 is obtained, insoluble in dilute acids, but soluble to an appreciable extent in concentrated hydrochloric acid.

Tungstic acid must always be washed with water which contains acid or a dissolved salt, as otherwise tungstic acid will form a pseudo-solution with pure water, so that a turbid filtrate will be obtained (cf. pp. 58, 134 and 231).

Phosphoric acid behaves differently toward solutions of the alkali tungstates than do the other mineral acids; it produces a white precipitate soluble in an excess of phosphoric acid; a complex phosphotungstic acid is formed, e.g., $Na_3PO_4 \cdot 12\ WO_3$. If the solution of an alkali tungstate is boiled with free tungstic acid, the latter gradually goes into solution, forming a metatungstate:

$$Na_2WO_4 + 3\ WO_3 = Na_2W_4O_{13}.$$

Mineral acids cause no precipitation in solutions of metatungstates. If the solution is boiled with an excess of acid, the soluble metatungstic acid is gradually changed to insoluble, ordinary tungstic acid, which is then precipitated. The addition of cinchonine hydrochloride greatly hastens the formation of insoluble tungstic acid in acid solutions.

2. H_2S produces no precipitation in acid solutions.

3. $(NH_4)_2S$ gives no precipitation in a solution of an alkali tungstate, but if the solution is afterward acidified, light-brown tungsten trisulfide, WS_3, is precipitated, which has the property of forming colloidal solutions with pure water, but is insoluble in hydrochloric acid. The precipitate redissolves in ammonium sulfide.

4. **Reducing Agents.** — If the solution of an alkali tungstate is treated with HCl and zinc, the tungstic acid at first precipitated by the HCl is soon turned to a beautiful blue color, owing to the formation of WCl_5.

$SnCl_2$ produces a yellow coloration at first, but on adding HCl and warming, a beautiful blue precipitate is obtained. This is one of the most sensitive tests for tungstic acid.

5. **Mercurous Nitrate** precipitates white mercurous tungstate from neutral solutions.

* The presence of tartaric acid prevents the precipitation.

6. **Lead Acetate,** barium chloride and silver nitrate also precipitate white tungstates from neutral solutions.

7. **Potassium Ferrocyanide** and a little acid give a brownish-red solution and a precipitate of the same color.

8. **Ferrous Sulfate** gives a yellowish brown precipitate and the precipitate is not turned blue by acid (cf. molybdenum).

9. Organic acids (citric, tartaric, etc.) form complex ions with tungstic acid and prevent its precipitation.

Reactions in the Dry Way

The salt of phosphorus bead is colorless in the oxidizing flame, and blue in the reducing flame, becoming blood red on the addition of a little $FeSO_4$.

SELENIUM, Se. At. Wt. 79.2. Sp. Gr. = 4.28–4.5. M. Pt. = 217–220° C.

Occurrence. — Although selenium is quite widely distributed in nature, it is invariably found in very small amounts, usually replacing sulfur, forming isomorphous compounds with lead, silver, copper, and mercury; clausthalite, PbSe; berzelianite, $(CuAgTl)_2Se$; naumannite, $(Ag_2Pb)Se$; tiemannite, HgSe; lehrbachite, (Pb,Hg)Se; onofrite, Hg(SeS); eucairite, $(Ag,Cu)_2Se$. It is also found in small amounts in many varieties of pyrite and chalcopyrite, and indeed the small quantities which are found in these minerals form the chief source of the selenium of commerce. By roasting these minerals (as in the manufacture of sulfuric acid) all of the selenium is volatilized, and is consequently deposited in the lead chambers as a mud from which it is extracted with a solution of potassium cyanide and afterwards precipitated with acid:

$$KCN + Se = KCNSe \quad \text{and} \quad KCNSe + HCl = HCN + KCl + Se.$$

Selenium, like sulfur, exists in several allotropic forms. The vitreous modification, *α-selenium*, dissolves slowly but completely in carbon disulfide. Red *β-selenium* is obtained by reducing a cold solution of selenious acid with sulfurous acid and is somewhat less soluble in carbon disulfide. The carbon disulfide solution of selenium reacts with metallic mercury and black mercury selenide precipitates. By heating *red* selenium with hot water for some time, it is changed into *black γ-selenium*, and is then *insoluble* in carbon disulfide.

On being heated in the air, selenium burns with a bluish flame (giving off an odor similar to that of rotten radishes) forming white, crystalline selenium dioxide, SeO_2, which will sublime on being heated in a stream

of oxygen. Selenium forms one oxide, SeO_2, and two acids: selenious acid, H_2SeO_3, and selenic acid, H_2SeO_4.

The vapors of selenium dioxide are yellow.

Heated in hydrogen, gaseous hydrogen selenide, H_2Se, is formed which behaves like hydrogen sulfide in its reactions.

Selenious acid, H_2SeO_3, is obtained in the form of long, colorless needles by oxidizing selenium with nitric acid, concentrated sulfuric acid or aqua regia,* or by dissolving its anhydride, SeO_2, in water. Unlike sulfurous acid, it is not changed on standing in the air into selenic acid; but, on the contrary, is reduced by dust, etc., to red selenium. The acid is dibasic, and forms salts in which either one or both of the hydrogen atoms are replaced by metal.

The acid salts are all soluble in water, but the neutral salts are all insoluble with the exception of those of the alkalies.

Selenic acid, H_2SeO_4, is obtained in solution by conducting chlorine into water which contains either suspended selenium or dissolved selenious acid:

$$Se + 3\,Cl_2 + 4\,H_2O = H_2SeO_4 + 6\,HCl.$$

Sodium selenate is obtained by fusing selenium with sodium carbonate and potassium nitrate. Selenic acid is a dibasic acid and behaves similarly to a peroxide, evolving chlorine when boiled with concentrated hydrochloric acid, being reduced to selenious acid:

$$H_2SeO_4 + 2\,HCl = H_2O + H_2SeO_3 + Cl_2\uparrow.$$

Reactions in the Wet Way

(*a*) *Selenious Acid*

A solution of either potassium selenite or of free selenious acid should be used.

1. **H_2S** produces a lemon-yellow precipitate, consisting of selenium and sulfur, from solutions in water or in dilute hydrochloric acid:

$$H_2SeO_3 + 2\,H_2S = 3\,H_2O + Se + 2\,S.$$

The precipitate is reddish yellow when formed in hot solutions.

The precipitate is soluble in ammonium sulfide.

2. **Reducing Agents.**

SO_2 precipitates red selenium. The solution may be hot or cold, and contain little or much hydrochloric or sulfuric acid; by long boiling the precipitate turns grayish black.

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* If a solution of selenium in aqua regia is evaporated, considerable selenium is lost by volatilization; the addition of KCl or NaCl to the solution prevents such loss.

$SnCl_2$ precipitates red selenium even in the presence of considerable sulfuric acid.

$FeSO_4$ immediately precipitates selenium from concentrated solutions of selenious acid containing hydrochloric acid; from dilute solutions the precipitation takes place very slowly and incompletely if much sulfuric acid is present.

Hydroxylamine Hydrochloride precipitates selenium, from solutions of selenious acid containing sulfuric or hydrochloric acid, on long boiling; the precipitated selenium is red at first but finally becomes gray (difference from tellurium).

Hydrazine Hydrochloride precipitates selenium from hot acid and alkaline solutions; the selenium is red at first and finally gray.

Hydriodic Acid (KI and HCl) precipitates red selenium in the cold (difference from tellurium).

Zinc precipitates red selenium from acid solutions: the zinc becomes coated with Se and looks as if covered with Cu.

3. **$BaCl_2$** precipitates from neutral solutions white barium selenite. $BaSeO_3$, soluble in dilute acids.

4. **$CuSO_4$** produces a greenish-blue, crystalline precipitate (difference from selenic acid).

(*b*) *Selenic Acid*

A solution of potassium selenate should be used.

1. **H_2S** causes no precipitation unless the solution is boiled with hydrochloric acid. In the latter case the selenic acid is reduced first to selenious acid and then to selenium, which precipitates together with free sulfur.

2. **$BaCl_2$** gives a white precipitate of barium selenate, $BaSeO_4$, insoluble in water and in dilute acids, soluble, with evolution of chlorine, on being boiled with hydrochloric acid:

$$BaSeO_4 + 4\,HCl = BaCl_2 + H_2SeO_3 + Cl_2\uparrow + H_2O.$$

3. **$CuSO_4$** produces no precipitation.

4. **SO_2** does not reduce selenic acid except by long boiling with hydrochloric acid. The reduction takes places more readily with hydrazine.

Method for Testing Sulfuric Acid for Selenium[*]

Add 5 or 6 drops of the acid to be tested to a freshly-prepared solution of a little codeïn in sulfuric acid; if selenium is present, a green coloration will be apparent. The test is a very delicate one.

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[*] DRAGENDORFF, *Chem. Zentralbl.*, **1900**, 944.

Reactions in the Dry Way

All selenium compounds emit the odor of decayed radishes on being mixed with sodium carbonate and heated on charcoal before the blowpipe.

If a selenium compound is heated at the end of a thread of asbestos in the upper reducing flame of the Bunsen burner, it will be reduced to selenium; and if a test-tube filled with water is held above the flame, a red coating of selenium will be deposited upon the glass.* If a few drops of concentrated sulfuric acid † are placed in a larger test-tube (large enough to hold the smaller test-tube) and the tube on which the selenium is deposited is emptied and placed within the larger tube, the selenium will dissolve ‡ in the sulfuric acid, forming a green solution; but on the addition of water, red selenium will be reprecipitated (difference from tellurium):

$$\underset{\text{Green}}{SeSO_3} + H_2O = \mathbf{Se} + H_2SO_4.$$

TELLURIUM, Te. At. Wt. 127.5. Sp. Gr. = 6.1–6.4. M. Pt. = 452° C.

Occurrence. — Tellurium is a rarer element than selenium, always occurring in the form of a telluride,§ and usually combined with the noble metals: calaverite, $(Au,Ag)Te_2$; krennerite, $(Au,Ag)Te_2$; sylvanite, $(Au,Ag)Te_4$; nagyagite, $(Pb,Au)_{16}Sb_3(S,Te)_{24}$; coloradoite, HgTe; silver telluride, Ag_2Te; and often in small amounts in galena and copper ores. Emmonsite of Cripple Creek, Colorado, is a ferric tellurite with 70.71 per cent TeO_2 and 22.76 per cent Fe_2O_3. Tellurium itself is a bluish-white, brittle substance, which can be distilled in a stream of hydrogen. It burns in the air with a bluish-green flame, forming tellurium dioxide, TeO_2. It is insoluble in carbon disulfide and in hydrochloric acid but can be oxidized by means of nitric acid to tellurous acid. On being fused with potassium cyanide, out of contact with the air, it is changed to potassium telluride,

$$2\,KCN + \mathbf{Te} = K_2Te + (CN)_2\uparrow,$$

which dissolves in water, forming a cherry-red solution. If air is conducted through this solution, the tellurium is precipitated in the form of a black powder (difference from selenium):

$$2\,K_2Te + 2\,H_2O + O_2 = 4\,KOH + 2\,\mathbf{Te}.$$

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* Cf. p. 69.

† The sulfuric acid should be freed from water by heating in a platinum crucible to a temperature just below the boiling-point, and the crucible with its contents allowed to cool in a desiccator.

‡ Slowly in the cold, readily on warming.

§ These tellurides are sometimes regarded as tellurium alloyed with metal.

Tellurium may be separated from selenium by means of this last reaction. Fuse the two metals with potassium cyanide, extract the melt with water, and precipitate the tellurium by passing a current of air through the solution; precipitate the selenium from the filtrate by acidifying with hydrochloric acid. Tellurium forms two oxides: TeO_2 and TeO_3.

Tellurium dioxide (the anhydride of tellurous acid) is usually obtained in the form of a white mass, which melts on gentle heating, forming a yellow liquid. Tellurium dioxide does not sublime (difference from selenium). It is scarcely soluble at all in water, is slightly soluble in ammonia and in dilute acids, but readily soluble in concentrated acids or in caustic potash solutions. TeO_2 dissolves in fairly concentrated sulfuric acid, forming the basic sulfate, $Te_2O_3 \cdot SO_4$, while with nitric acid it forms the basic nitrate, $Te_2O_3(OH)NO_3$. Both of these compounds are hydrolized readily, forming insoluble tellurous acid; the latter in turn loses water and forms the anhydride.

On dissolving TeO_2 in caustic potash, potassium tellurite, K_2TeO_3, is obtained. *Only the alkali tellurites are soluble in water.*

Tellurium trioxide (telluric anhydride) is formed by heating telluric acid. It is a yellow powder, insoluble in water and nitric acids, scarcely affected by boiling with concentrated hydrochloric acid, but is readily dissolved by boiling with a concentrated solution of potassium hydroxide (but not by sodium hydroxide), forming potassium tellurate.

Telluric acid, $H_2TeO_4 + 2\,H_2O$, is a very weak acid, obtained by oxidizing tellurous acid with chromic acid, and precipitating the telluric acid by the addition of concentrated nitric acid. The acid forms a colorless crystalline mass, is readily soluble in water, and is converted by means of concentrated hydrochloric acid into tellurous acid, with evolution of chlorine. The acid dissolves readily in caustic potash (or soda) solution, forming the readily soluble alkali tellurate, which reacts strongly alkaline in aqueous solution.

By gently heating the hydrated telluric acid, the anhydrous acid, H_2TeO_4, is obtained in the form of a white powder and is totally different from the hydrated acid. The latter is *soluble* in water and in caustic alkalies, and is *completely reduced* by boiling with concentrated hydrochloric acid; but the anhydrous acid is *insoluble* in water and in concentrated sodium hydroxide solution, and is only very slightly attacked by boiling, concentrated hydrochloric acid, although readily soluble in warm potassium hydroxide solution.

Only the alkali tellurates are soluble in water; the others are usually obtained in the form of amorphous precipitates soluble in acids.

Reactions in the Wet Way

(*a*) *Tellurous Acid*

A solution of potassium tellurite, K_2TeO_3, should be used.

1. **H_2S** precipitates from acid solutions brown TeS_2, which is readily soluble in ammonium sulfide. The precipitate decomposes easily into tellurium and sulfur.

2. **Reducing Agents.**

SO_2 precipitates tellurium completely from *dilute* hydrochloric acid solutions in the form of a black powder, even in the presence of tartaric acid; but from a solution containing considerable hydrochloric acid no tellurium is precipitated even on boiling (difference from selenium). The separation of the selenium from tellurium can be accomplished in hydrochloric acid, sp. gr. 1.18.

$SnCl_2$ or **Zn** causes black tellurium to precipitate from solutions which are not too acid.

H_3PO_3 precipitates the tellurium only from concentrated solutions, not at all from cold dilute solutions.

$FeSO_4$ reduces neither tellurous nor telluric acids (difference from selenium).

Hydroxylamine Hydrochloride produces no precipitate in solutions of tellurous acid containing mineral acids, but precipitates tellurium completely by boiling the ammoniacal solutions for a long time.

$$2\,NH_2OH + TeO_3^{--} + 2\,H^+ \rightarrow 4\,H_2O + N_2O\uparrow + \mathbf{Te}.$$

Hydrazine Hydrochloride precipitates black tellurium both from acid and ammoniacal solutions:

$$N_2H_4 \cdot 2\,HCl + TeO_3^{--} \rightarrow 3\,H_2O + N_2\uparrow + \mathbf{Te} + 2\,Cl^-.$$

Hydriodic Acid (KI and HCl) produces no precipitation, but merely a reddish-brown coloration that turns light yellow on boiling (difference from selenium).

Zinc (or Fe, Sb, Sn, Cd, Hg, Pb, Cu, etc.) precipitates black tellurium.

3. **HCl** produces a white precipitate of H_2TeO_3.

4. **Magnesia Mixture** gives a white, amorphous precipitate of magnesium tellurite. (With selenious acid a crystalline precipitate of magnesium selenite is formed.)

5. **Disodium Phosphate** and **Barium Chloride** give white precipitates.

(*b*) *Telluric Acid*

A solution of potassium tellurate should be used.

1. **HCl** causes no precipitation; but if the solution is boiled chlorine is evolved, and on dilution with water tellurous acid is precipitated.

2. **H_2S** and reducing agents have the same effect upon hot solutions of tellurates as upon tellurites; in the cold, no precipitate is formed (tellurium can be separated from heavy metals by hydrogen sulfide in the cold).

3. **Lead Salts** precipitate difficultly soluble lead tellurate.

4. **Hydrazine Hydrochloride** precipitates all the tellurium as a black powder by long boiling of the acid or alkaline solution:

$$3(N_2H_4 \cdot 2HCl) + 2TeO_4^{--} \rightarrow 8H_2O + 2H^+ + 6Cl^- + 3N_2\uparrow + 2\mathbf{Te}.$$

Detection of Selenium and Tellurium in Ores

Principle. — The finely powdered, dry ore is heated in a current of chlorine; the chlorides of sulfur, selenium, arsenic, antimony and iron are volatilized and may be absorbed in dilute hydrochloric acid.

Procedure. — Place the finely powdered, dry mineral in a porcelain boat, push this into a tube of difficultly fusible glass and connect the tube on one side with the wash-bottle and on the other side with a 10-bulb Meyer tube.

Prepare chlorine gas from a Kipp generator containing chloride of lime and hydrochloric acid, wash the gas by passing it through a bottle containing water and dry it by passing it through concentrated sulfuric acid. Pass the chlorine gas through the tube and when all the air has been expelled, begin heating the substance, at first very gently. Fumes quickly begin to form, showing that the action of chlorine upon the substance has started. Soon vapors of sulfur chloride, S_2Cl_2 (B. P. 64°) begin to condense in the front end of the tube in the form of drops; drive these over into the receiver by carefully heating the tube. As the temperature is raised a little, a white sublimate of selenium chloride, $SeCl_4$ (B. P. 200°) forms in the front end of the tube; drive this over into the receiver in the same way. Now heat the boat hotter and soon brown vapors of ferric chloride will be evolved, some of these will condense, forming glistening scales which must also be driven over into the receiver. Continue heating until finally no more vapors are evolved. Transfer the contents of the 10-bulb tube to a porcelain dish, add 0.5 gm. of potassium chloride to prevent loss of selenium chloride by volatilization, and evaporate the solution to dryness on the water-bath. Dissolve the residue in as little hydrochloric acid as possible and treat the solution with stannous chloride. If tellurium is present a black precipitate is obtained which may also contain selenium. Filter through an asbestos filter, wash the residue with dilute hydrochloric acid, place the filter and asbestos in a small test-tube, boil it with concentrated hydrochloric acid until no more black spots are visible in the asbestos, dilute with water and filter. Evaporate this filtrate to dryness on the water-bath, dissolve the residue in 10 cc. of HCl, sp. gr. 1.175, and pass SO_2 gas into the hot solution. Filter off any precipitate of red selenium that may form. Dilute the filtrate with considerable water and again pass SO_2 into the hot solution, which should precipitate the tellurium as a black powder. Identify the selenium and the tellurium by the dry reactions given on p. 555 and below.

Reactions in the Dry Way

Metallic tellurium is formed by heating any telluride in the upper reducing flame, and can be collected on the lower surface of a test-tube, which is filled with water, in the form of a black film, soluble in concentrated sulfuric acid. The latter solution is of a carmine-red color (difference from selenium); on the addition of water black tellurium is deposited:

$$\underset{\text{Carmine red}}{TeSO_3} + H_2O = \mathbf{Te} + H_2SO_4.$$

THE PLATINUM METALS

PLATINUM, PALLADIUM, RHODIUM, OSMIUM, RUTHENIUM AND IRIDIUM

Platinum has been described already on p. 283

PALLADIUM, Pd. At. Wt. 106.7. Sp. Gr. = 11.8. M. Pt. = 1550° C.

Occurrence. — The platinum metals form an isodimorphous group, but only in the case of palladium are both forms known — the isometric and the hexagonal:

(*a*) Isometric System.	(*b*) Hexagonal System.
Platinum (Pt, Fe).	Iridosmium (Sysserskit) (Ir, Os).
Iridium (Ir, Pt).	Osmiridium (Newjanskit) (Ir, Os, Pt, Rh, Ru) or (Os, Ir, Rh).
Platinum iridium (Pt, Ir, Rh).	
Palladium (Pd, Pt, Ir).	**Palladium (Pd,** Pt, Ir).

Properties. — Rolled, hammered, or cast palladium possesses an almost silver-white color, but when precipitated from solutions it is in the form of a black powder. If it is suspended in water when in the finely divided form, it is transparent with a reddish color. Palladium has the lowest melting-point of all the platinum metals. On being heated in the air, it appears bluish, owing to the formation of Pd_2O; the latter, however, is decomposed by stronger heating.

Finely divided palladium has the very characteristic property of being able to absorb almost 700 times its own volume of hydrogen, and possesses consequently a very strong catalytic action. If hydrogen and oxygen (air) are conducted at the same time over some gently-ignited, finely-divided, metallic palladium, the hydrogen is burnt to water, and in the same way carbon monoxide may be changed to carbon dioxide. Methane, however, is only decomposed by igniting the palladium more strongly, so that this gives us a method for separating methane from a mixture of H and CO (cf. Vol. 2, Gas Analysis).

Colloidal palladium preparations show marked catalytic effects. Thus by passing hydrogen gas into solutions of unsaturated organic compounds a direct reduction (hydrogenation) often takes place if a little colloidal palladium is present.

Palladium forms two oxides, both of which possess strongly basic

properties: PdO and PdO_2. From the former the palladous, and from the latter the palladic, compounds are derived. The palladous compounds are much more stable than the palladic compounds, and the latter constantly exhibit the tendency to change into the former.

Behavior towards Acids: Although the other platinum metals are attacked by no acid except aqua regia, palladium is dissolved slowly by warm nitric acid (also in the cold when it is alloyed with other metals such as Cu, Ag, etc.), forming a brown solution of $Pd(NO_3)_2$.

Finely divided, precipitated palladium is soluble in hydrochloric acid when exposed to the action of air at the same time, and less readily soluble in sulfuric acid. It is readily attacked by fusing with potassium pyrosulfate, forming soluble palladium sulfate, $PdSO_4$.

The best solvent for palladium is aqua regia.

By dissolving finely divided palladium in hydrochloric acid, palladous chloride is formed; or, better, by dissolving the metal in aqua regia, in which case a mixture of palladous and palladic chlorides is at first obtained. If this solution, however, is evaporated to dryness, palladic chloride loses chlorine and is completely changed into palladous chloride, so that on treating the residue with water a solution of palladous chloride is obtained. Since palladic chloride is decomposed completely by evaporation, it is evident that palladic chloride cannot exist in hot solutions.

Reactions in the Wet Way

(*a*) *Palladous Compounds*

Use a solution of palladous chloride, $PdCl_2$

1. **H_2S** precipitates black palladous sulfide from acid and neutral solutions. The precipitate, PdS, is insoluble in ammonium sulfide, but soluble in boiling hydrochloric acid, or more readily in aqua regia.

Palladous sulfide is soluble in potassium thiocarbonate solution and is not reprecipitated by means of carbon dioxide. (Lead sulfide does not dissolve in potassium thiocarbonate and mercury sulfide is reprecipitated by carbon dioxide.)

2. **KOH** or **NaOH** precipitates a brown basic salt, soluble in an excess of the reagent. If the solution is acidified with HCl, then KOH produces no precipitate (difference from platinum).

3. **Na_2CO_3** produces a brown precipitate of palladous hydroxide, $Pd(OH)_2$, soluble in excess but reprecipitated on boiling.

4. **NH_4OH** gives a flesh-colored precipitate of $[Pd(NH_3)_2Cl_2]_n$ *

* This compound is an isomer of palladosamine chloride, and is often written thus: $PdCl_2, Pd(NH_3)_4Cl_2$.

soluble in an excess of ammonia, forming a colorless solution (containing palladodiamine chloride, $Pd(NH_3)_4Cl_2$), from which yellow crystalline palladosamine chloride, $Pd(NH_3)_2Cl_2$, is precipitated on the addition of hydrochloric acid. The latter compound is difficultly soluble in dilute hydrochloric acid and is used for the preparation of pure palladium.

In a solution of palladous nitrate, ammonia causes no precipitation, but forms colorless palladodiamine nitrate, $Pd(NH_3)_4(NO_3)_2$.

5. **NH_4Cl.**—If a solution of palladous chloride or of sodium-palladous chloride is treated with ammonium chloride and evaporated to dryness on the water-bath, the residue is soluble in a very little water. If the solution is acidified with nitric acid, gradually all the palladium is precipitated as red $(NH_4)_2[PdCl_6]$ (difference from platinum).

6. **KCl**, when added to a concentrated solution, causes the precipitation of difficultly-soluble, reddish-brown $K_2[PdCl_4]$ (octahedrons).

7. **HI** or **KI** produces a black precipitate of palladous iodide, even in very dilute solutions. The precipitate is insoluble in water, alcohol, ether, and HI, but soluble in KI and NH_3. (This and the following reaction are characteristic of palladium.)

8. **$Hg(CN)_2$** produces a yellowish-white gelatinous precipitate of palladous cyanide, $Pd(CN)_2$, difficultly soluble in HCl, readily soluble in KCN and NH_3. On being ignited, the spongy metal remains.

9. **Nitroso-β-naphthol** (a saturated solution in 50 per cent acetic acid) gives a voluminous, brown precipitate of $Pd(C_{10}H_6NO_2)_2$ even in the most dilute solutions (difference from platinum).

10. **Reducing Agents.** — H_2SO_3, formic acid, HCOOH, Zn, Fe, $FeSO_4$, Cu_2Cl_2,* alcohol, and CO † reduce palladium salts to the metal itself.

In the presence of HCl, stannous chloride forms at first a red, then a brown, and finally a green, solution; but in the absence of the acid, $SnCl_2$ causes a partial reduction to the metal and the solution turns green.

11. **Acetylene** precipitates palladous acetylide, which is soluble in ammonia, potassium cyanide and sodium bisulfite solutions.

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* In the presence of considerable NaCl or HCl there is no reduction with Cu_2Cl_2.

† $PdCl_2 + CO + H_2O = 2\,HCl + CO_2\uparrow + Pd$. This reaction enables one to detect small amounts of CO in gas mixtures; e.g., in the air. For this purpose the gas is led through a narrow glass tube into 10 cc. of a solution which contains 1 mg. of $PdCl_2$ and 2 drops of dilute HCl. If CO is present, black Pd will be deposited, and the solution will become decolorized little by little. (Potain and Drouin, *Compt. rend.*, **126**, 938.) If too much HCl is present the reduction will not take place unless $NaC_2H_3O_2$ is added.

12. **Sodium Hydroxide** precipitates a brown, basic salt which is soluble in a large excess of alkali.

13. **Potassium Nitrite** gives a yellow, crystalline precipitate in solutions which are not too dilute.

14. **Potassium Thiocyanate** gives no precipitate with palladium solutions (difference from copper).

15. **Dimethylglyoxime** gives a yellow precipitate easily dissolved by ammonia or potassium cyanide solution; the precipitate is only slightly soluble in 50 per cent alcohol and dilute acids. Gold and platinum give similar tests but the other platinum metals do not.

(*b*) *Palladic Compounds*

These give the same reactions as palladous compounds, on account of their being readily changed into the latter. The most characteristic reaction is based upon the insolubility of the ammonium salt of chloropalladic acid. If a concentrated, cold solution of palladous chloride is shaken with chlorine water and then treated with ammonium chloride, a red crystalline precipitate of $(NH_4)_2[PdCl_6]$ is soon formed.

Reactions in the Dry Way

All palladium compounds are decomposed on ignition, leaving behind the metal, which is soluble in nitric acid or in aqua regia, and the solution thus obtained can be tested by the above reactions.

RHODIUM, Rh. At. Wt. 102.9. Sp. Gr. = 12.6. M. Pt. = 1920°?

Properties. — Rhodium possesses the color and luster of aluminium; it is more infusible than platinum and melts at about 1920°; on cooling the hot metal it sputters and appears bluish, owing to oxidation. The solubility of rhodium depends entirely upon the fineness of the material.

When precipitated from a solution of its chloride by means of formic acid or other reducing agents at a temperature not exceeding 100°, it exists in an extremely-finely-divided state (rhodium black) and dissolves readily in boiling, concentrated sulfuric acid, or more readily in aqua regia. If, however, the finely-divided metal is ignited strongly, it becomes (like the compact metal) almost insoluble in aqua regia.

If rhodium is alloyed with large amounts of other metals (Pb, Zn, Bi, Cu, etc.), it is left in a finely-divided condition after treatment of the alloy with acids, and is consequently soluble in aqua regia. When it is alloyed with much platinum or palladium a considerable amount

of rhodium will dissolve in aqua regia; but when it is alloyed with a little platinum, most of the rhodium and a part of the platinum remain undissolved.

On being fused with potassium pyrosulfate, potassium rhodium sulfate is formed, which dissolves in water, forming a yellow solution, but becomes red on the addition of HCl.

Rhodium forms three oxides: rhodous oxide, RhO; rhodic oxide, Rh_2O_3; and rhodium peroxide, RhO_2; all possess a well-defined basic nature. The sesquioxide, Rh_2O_3, alone * forms a series of salts, of which sodium rhodium chloride is the most important for the analytical chemist; when in this form it is easiest to bring rhodium into solution. This salt is prepared by mixing the finely-divided metal very intimately with twice as much dry sodium chloride, placing it in a porcelain boat and gently igniting it in a current of moist chlorine gas. The salt thus formed has the composition $Na_3[RhCl_6]$ and is soluble in water (45 parts of water dissolve 1 part of the salt). From this solution large, dark-red, glistening triclinic prisms of $Na_3[RhCl_6] + 9\ H_2O$ can be crystallized out.

Reactions in the Wet Way

Use a solution of sodium rhodium chloride $Na_3[RhCl_6]$.

1. **H_2S** precipitates (very slowly in the cold, but much more quickly on warming) black rhodium sulfide, Rh_2S_3 or $Rh(SH)_3$; insoluble in $(NH_4)_2S$, soluble in strong nitric acid, bromine or aqua regia. Alkali monosulfide added in excess precipitates rhodium alkali sulfide, decomposable by water.

2. **KOH** and **NaOH** produce at first no precipitate; but after standing some time a yellow precipitate of rhodium hydroxide, $Rh(OH)_3 + H_2O$, separates out. The precipitate is soluble in an excess of the reagent, but it is reprecipitated on boiling in the form of brownish-black $Rh(OH)_3$.

In a solution of potassium rhodium sulfate, KOH precipitates the yellow compound immediately.

On adding KOH to a solution of rhodium chloride, at first no precipitate is produced; but on the addition of a little alcohol brownish-black rhodium hydroxide is deposited.

3. **NH_4OH** produces (in concentrated solutions and after standing some time) a yellow precipitate of chlorpurpureorhodium chloride, $Rh(NH_3)_5Cl_3$, insoluble in hydrochloric acid.

* A sodium rhodium sulfite of the formula $4\ RhSO_3 \cdot 6\ Na_2SO_3 \cdot 9\ H_2O$ was prepared by Bunsen.

4. KNO_2, on being warmed with sodium rhodium chloride solution, causes the precipitation of difficultly soluble, orange-yellow $K_3[Rh(NO_2)_6]$, soluble in HCl.

5. **Reducing Agents.** — Formic acid, in the presence of ammonium acetate, precipitates the black metal, as does zinc in the presence of acids. Hydroxylamine sulfate has no effect (difference from gold).

Reactions in the Dry Way

All rhodium compounds are reduced to metal on being heated in a stream of hydrogen, or by heating on charcoal with sodium carbonate before the blowpipe. The metal is easily recognized by its insolubility in aqua regia, its being brought into solution by fusing with potassium pyrosulfate and then treating with water, and by the formation of the brown hydroxide when KOH and a little alcohol are added to the solution thus obtained.

OSMIUM, Os. At. Wt. 190.9. Sp. Gr. = 21.3–22.48. M. Pt. = about 2700°

Osmium and ruthenium are distinguished from the other platinum metals by their forming volatile oxides.

Properties. — The compact metal possesses a bluish-white color, very similar to zinc, and is the heaviest of all metals. It can be melted by heating in an electric furnace.* Very finely-divided osmium is oxidized by the air † at ordinary temperatures, and at about 400° C. it ignites and burns rapidly to OsO_4, which is volatile at 100° C. The denser the metal the higher the temperature necessary to effect the oxidation.

Behavior towards Acids. — In the compact condition osmium is insoluble in all acids; but in the finely-divided state (as obtained by treating its zinc alloy with nitric acid) it is soluble in nitric acid, more soluble in aqua regia, and most soluble in fuming nitric acid, forming osmium tetroxide; the latter can be separated from the solution by distillation.

Compact osmium is brought into solution by fusing with NaOH and either KNO_3 or $KClO_3$. The melt contains a salt of perosmic acid (OsO_4).

Osmium forms five oxides:

OsO, Osmious oxide, grayish-black, insoluble in acids	Os_2O_3, Osmium sesquioxide, black, insoluble in acids	OsO_2, Osmic oxide, black-gray, insoluble in acids
$[OsO_3]$, Osmic acid, known only in derivatives	OsO_4. Perosmic acid anhydride, colorless needles soluble in water	

* F. Mylius and R. Dietz, *Ber.*, **1898**, 3187.

† Cf. Ot. Sulc, *Z. anorgan. Chemie*, **19**, 332.

Osmium tetroxide, OsO_4, (the anhydride of perosmic acid), is the most important osmium compound in the eyes of the analytical chemist and is obtained by the oxidation of the substance in the air by dissolving the finely-divided metal in fuming nitric acid or in aqua regia, or by fusing with NaOH and KNO_3 or $KClO_3$, treating the melt with nitric acid and distilling. Osmium tetroxide is a colorless, crystalline mass which sublimes at a comparatively low temperature and melts, forming colorless vapors at 100° C. The vapor has a chlorine-like odor, attacks the mucous membrane, and is poisonous.

The chlorides of osmium can be obtained only in the dry way; $OsCl_2$, $OsCl_3$, $OsCl_4$ are known. The potassium salt of the hypothetical chlorosmic acid, H_2OsCl_6, forms dark-red octahedrons, soluble in water and decomposed by boiling the solution. By heating finely-divided osmium with KCl in a current of chlorine, $K_2[OsCl_6]$ is formed; it dissolves in cold water, forming a red solution.

Reactions in the Wet Way

Use a solution of $K_2[OsCl_6]$

1. If a solution of osmium chloride is treated with dilute nitric acid, the mixture distilled from a small retort, and the vapors received in caustic soda solution, the latter will be colored yellow, owing to the formation of potassium osmiate. If this solution is now acidified, osmium tetroxide is set free, and can be recognized by its very penetrating odor. On adding a little sodium thiosulfate to the acid solution and warming, a brown precipitate of osmium sulfide is formed.

2. **H_2S** precipitates brownish-black osmium sulfide, insoluble in ammonium sulfide.

3. **KOH, NH_4OH** or **K_2CO_3** precipitates reddish-brown osmium hydroxide $Os(OH)_4$.

4. **Reducing Agents.** — If the solution of the chloride is treated with tannic acid and alcohol and a little hydrochloric acid is added, it is colored dark-blue, owing to the formation of osmium dichloride, $OsCl_2$; KI colors the solution a deep reddish-purple.

5. **Indigo** is decolorized by solutions containing OsO_4. Ferrous sulfate precipitates black osmium dioxide; stannous chloride produces a brown precipitate soluble in HCl, forming a brown solution.

Reactions of Perosmic Acid

Osmium tetroxide melts when added to boiling water and dissolves slowly. The solution is colorless, does not react acid but smells unpleasantly.

1. **KOH** added in excess to the concentrated solution colors it yellow. If this alkaline solution is boiled, the greater part of the tetroxide distills off (very charac

teristic) and the remainder decomposes into oxygen and potassium osmiate, K_2OsO_4; upon long boiling osmium tetroxide, osmic hydroxide and potassium hydroxide are formed from it.

2. **Indigo Solution** is decolorized.

3. **Potassium Iodide** reduces the perosmic acid in acid solutions. If 2 cc. of one per cent potassium iodide solution and 20 drops of concentrated sulfuric acid are mixed with one drop of osmium salt solution, a green solution of H_2OsI_4 is obtained; the colored compound can be shaken out with ether.

4. KNO_2 forms red crystals of potassium osmiate. The same compound can be obtained by reducing osmium tetroxide solution with alcohol.

5. SO_2 reduces perosmic acid. As the reduction proceeds, the color changes to yellow, reddish brown, green and finally indigo blue.

6. $FeSO_4$ precipitates black osmium dioxide.

7. $SnCl_2$ gives a brown precipitate which dissolves in hydrochloric acid to form a brown solution.

8. **Zinc,** and other metals, in the presence of acid causes precipitation of metallic osmium.

9. H_2S at first colors the solution dark brown; on adding acid a dark brown precipitate of osmium tetrasulfide, OsS_4, is obtained which is insoluble in alkali hydroxide, carbonate, or sulfide.

Reactions in the Dry Way

All osmium compounds are reduced to metal on being heated in a stream of hydrogen.

RUTHENIUM, Ru. At. Wt. 101.7. Sp. Gr. = 12.26, crystallized; 11.0, fused. M. Pt. = above 1950°

Properties. — Ruthenium can be obtained in the form of a dark gray or black powder, and in the form of bright porous sticks; it is brittle, can be powdered, and is melted in the oxyhydrogen flame.

On being melted, a part of the ruthenium is oxidized to ruthenium tetroxide, a volatile substance having a penetrating odor similar to that of OsO_4. The molten metal spurts on cooling.

Behavior towards Acids. — Ruthenium is practically insoluble in all acids, even aqua regia. By fusing with KOH and KNO_3 (or $KClO_3$) it is oxidized to potassium rutheniate, $K_2[RuO_4]$.

On heating with KCl in a current of chlorine, soluble $K_2[RuCl_6]$ is formed. The greenish-black melt dissolved in water gives an orange-yellow solution which colors the human skin black. Gradually on standing, or immediately on boiling, a black, voluminous colloidal precipitate forms (sensitive reaction). Ruthenium is unaffected by fusing with potassium pyrosulfate.

It forms the following oxides:

$$RuO,\ Ru_2O_3,\ RuO_2,\ [RuO_3],\ [Ru_2O_7],\ RuO_4.$$

The most important of the oxides is RuO_4. It is formed:

(*a*) By roasting the metal itself, or its oxide, above 1000° C. (osmium forms the volatile tetroxide at 400° C.).

(*b*) By fusing the metal with KOH and KNO_3 in a silver crucible, dissolving the melt in water, saturating the cold solution with chlorine gas, and distilling the solution from a small retort:

$$K_2RuO_4 + Cl_2 = 2\,KCl + RuO_4.$$

(*c*) By treating the solution of potassium ruthenium chloride with KOH and Cl, and subsequently distilling.

(*d*) By distilling potassium ruthenium chloride with $KClO_3$ and HCl.

By distilling a dilute solution after the addition of nitric acid, no RuO_4 will be evolved * (difference from osmium).

Ruthenium tetroxide forms gold-yellow, glistening, orthorhombic needles that are volatile and emit a characteristic odor; it boils at 100° C. and is only slightly soluble in water. It is changed by the addition of alcohol and HCl into ruthenium trichloride, $RuCl_3$ (or sesquichloride, Ru_2Cl_6). If the solution of the latter salt is made ammoniacal, treated with sodium thiosulfate and warmed, an intense reddish-violet coloration will be produced. (This is a very sensitive and characteristic reaction.)

On treating a solution of potassium rutheniate with nitric acid, black $Ru(OH)_3$ is precipitated; it dissolves in hydrochloric acid, forming a yellow solution of $RuCl_3$.

Reactions in the Wet Way

Use a solution of $RuCl_3$

1. **H_2S** produces no precipitation at first, but after some time the solution becomes azure-blue, and brown ruthenium sulfide is precipitated (very sensitive and characteristic).

2. **$(NH_4)_2S$** precipitates the brownish-black sulfide, difficultly soluble in an excess of the reagent.

If a ruthenium solution is made slightly alkaline with sodium carbonate and is boiled a short time with potassium nitrite, then, after cooling, a little ammonium sulfide will give a beautiful, carmine-red color which eventually turns to brown. More ammonium sulfide gives a brown precipitate.

3. **KOH** and **NaOH** precipitate black ruthenium hydroxide, $Ru(OH)_3$, soluble in acids but insoluble in alkalies.

* In the presence of concentrated nitric acid, however, RuO_4 is formed:

$$2\,K_2RuO_4 + 4\,HNO_3 = 4\,KNO_3 + Ru(OH)_4 + RuO_4.$$

4. **KCNS**, in the absence of other platinum metals, produces gradually a red, then a purple, and on warming a violet, coloration (very characteristic).

5. **KNO_2** imparts an orange-yellow color to the solution, owing to the formation of $K_3[Ru(NO_2)_6]$, becoming a beautiful dark red on the addition of a little colorless ammonium sulfide; on adding more ammonium sulfide, brown ruthenium sulfide is precipitated.

6. **Zinc** at first colors the solution of the chloride azure blue, but subsequently the solution is decolorized and ruthenium itself is precipitated.

7. **Hydroxylamine** reduces ruthenium tetrachloride to ruthenium trichloride (difference from platinum).

8. **KI** precipitates a black iodide; the reaction is aided by heating.

IRIDIUM, Ir. At. Wt. 193.1. Sp. Gr. = 22.4. M. Pt. = 2300°?

Properties. — When produced by the ignition of iridium ammonium chloride, iridium is obtained in the form of a gray, spongy mass, very difficultly soluble in aqua regia. After being strongly ignited, it is almost completely insoluble in aqua regia.

The metal, although brittle, is similar to platinum.

It is more soluble in aqua regia after it has been precipitated from solutions in a very finely-divided form by means of formic acid, or when it is alloyed with other metals (Au, Ag). The metal is unaffected by fusing with potassium pyrosulfate (difference from rhodium). It is oxidized by fusing with NaOH and KNO_3 in a silver crucible, but the compound formed (Ir_2O_3 combined with sodium) is only partly soluble in water. If the melt is treated with aqua regia, however, a dark-red solution of $Na_2[IrCl]_6$ will be obtained.

By heating the metal with NaCl in a current of chlorine, $Na_2[IrCl_6]$ is readily obtained which forms with water a reddish-brown solution.

Iridium forms the following oxides:

Ir_2O_3,?	IrO_2,	and the hydroxide	$Ir(OH)_4$.
Bluish black	Needles with a metallic luster		Indigo-blue powder

The dark color of the chlorides is very characteristic:

$IrCl_3$,*	$IrCl_4$.
Dark green and brown	Black

* According to W. PALMAER, *Z. anorg. Chem.*, **10**, 322-326 (1895), $IrCl_3$ and its double salts exist in two modifications: dark green and brown.

Reactions in the Wet Way

Use a solution of $Na_2[IrCl_6]$

1. **H_2S** at first decolorizes the solution, owing to the reduction of the tetrachloride to the trichloride, accompanied by the deposition of sulfur; subsequently brown Ir_2S_3 is precipitated, readily soluble in $(NH_4)_2S$.

2. **$(NH_4)_2S$** precipitates the same compound.

3. **NaOH**, on being added to the solution, changes the color from dark red to green; on warming the solution it is at first colored reddish and finally azure blue:

$$2\,IrCl_4 + 2\,NaOH = 2\,IrCl_3 + NaCl + H_2O + NaOCl.$$

If the solution is now acidified with HCl, a little alcohol* added and then some KCl, there will be no precipitation, because the $K_3[IrCl_6]$ formed is readily soluble in water and in KCl solution (difference from platinum).

If sodium hypochlorite or hypobromite is added to the alkaline solution, blue IrO_2 is formed.

4. **KCl** precipitates brownish-black potassium iridium chloride, $K_2[IrCl_6]$, insoluble in KCl and in alcohol, difficultly soluble in water.

5. **NH_4Cl** precipitates dark-red ammonium iridium chloride, $(NH_4)_2[IrCl_6]$, insoluble in a saturated solution of NH_4Cl.

If a solution of potassium or ammonium salt of H_2IrCl_6 in hot water is treated with potassium nitrite, the olive-green potassium or ammonium salt of H_3IrCl_6 is obtained:

$$K_2IrCl_6 + KNO_2 \rightarrow K_3IrCl_6 + NO_2\uparrow.$$

On cooling the salt crystallizes. If, however, an excess of potassium nitrite is added to the hot green solution, it turns yellow and finally a *white* precipitate is formed.

6. **Reducing Agents** usually change the solution to a greenish color, owing to the reduction of the tetrachloride to trichloride; or the solution is decolorized and the black, finely divided metal is deposited.

Thus if the solution is warmed with KNO_2, an olive-green coloration is produced:

$$IrCl_4 + KNO_2 = IrCl_3 + KCl + NO_2\uparrow.$$

If the solution is boiled for some time with an excess of KNO_2, it becomes yellow, and a part of the iridium separates out in the form of a yellowish-white precipitate, difficultly soluble in cold hydrochloric acid or in boiling water. The precipitate has the following composition: $3\,K_3[Ir(NO_2)_6] \cdot K_3[IrCl_6]$.

* The alcohol reduces NaOCl to NaCl.

Oxalic acid, ferrous sulfate, stannous chloride, and hydroxylamine reduce the tetrachloride to trichloride. Zinc reduces it to metal, and so does formic acid on warming in the presence of ammonium acetate. If considerable mineral acid is present the reduction takes place less readily.

Boiling with stannous chloride and adding an excess of caustic alkali gives a leather colored precipitate.

7. **Chlorine.** — If chlorine is conducted into a dilute solution of iridium tetrachloride, the latter becomes reddish-violet according to W. Palmaer, * after some time the red color disappears and the solution turns brown. The same red color has been observed by Foerster † at an iridium anode in sulfuric acid. According to Palmaer, the red color is due to the formation of an iridium compound having a higher valence than four.

Reactions in the Dry Way

On being fused with soda, the gray, brittle metal can be obtained by the action of the upper reducing flame. It is insoluble in aqua regia.

Separation of the Platinum Metals

The separation of the platinum metals is one of the most difficult tasks met with in analytical chemistry. If the metals are already in solution, the table on p. 572 can be used to advantage. If, however, the metals are present in a more compact form, it is quite difficult to bring them into solution.

In the latter case treat the metal in as finely divided condition as possible (filings, etc.) with aqua regia; this serves to dissolve the greater part of the platinum and palladium, as well as small amounts of rhodium and iridium. Dry the residue (osmium, ruthenium, rhodium, iridium, and small amounts of platinum and palladium), place it in a porcelain crucible and fuse for some time with ten times as much zinc (or lead) in a current of illuminating gas.‡ In this way the platinum metals are alloyed with the zinc. Allow the mass to cool in the stream of illuminating gas, and treat it with hydrochloric acid to dissolve out the zinc; this leaves the platinum metals behind in a finely divided state. Filter them off from the acid solution, dry and introduce them into a porcelain boat; place the boat in a tube made of difficultly fusible glass, and heat to dark redness in a stream of oxygen.

The greater part of the osmium escapes as osmium tetroxide; it is absorbed by the caustic soda solution and tested according to the table. Mix the residue inti-

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* *Z. anorg. Chem.*, **10** (1895), 358.

† *Z. Electrochem.*, **10**, 715.

‡ The operation can be very conveniently performed in a common clay pipe. The gas is conducted through the stem and ignited at the bowl. In this way the gas continually streams through the molten alloy, keeps it well stirred, and thereby yields a uniform alloy.

mately with sodium chloride and heat in a stream of moist chlorine gas. Dissolve the mass in water and examine it according to the table.

If lead were used instead of zinc in the above procedure, the alloy should be treated with dilute nitric acid, which dissolves the lead and the greater part of the palladium. Precipitate the lead with the calculated amount of sulfuric acid, and test the filtrate for palladium by transforming it into palladosamine chloride, and then into palladium cyanide. Treat the residue from the nitric acid treatment in the same way as when zinc is used.*

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* For more detailed directions for separating the platinum metals, consult the work of SAINTE-CLAIRE-DEVILLE, DEBRAY, and STAS: "Procés verbaux du comité internat. des poids et mesures," 1877–1878 and 1879.

ANALYSIS OF THE PLATINUM METALS *

The six platinum metals, in the presence of gold and mercury, are assumed to be present in solution as chlorides. *Place the solution in a small retort, treat with dilute HNO_3, heat to boiling, and conduct the vapors into NaOH solution.* The solution remaining in the retort contains the remaining metals.

DISTILLATE.

If the NaOH becomes yellow, Os may be present. *In this case acidify with HCl and try to detect the odor of OsO_4. Add a little $Na_2S_2O_3$, and heat the solution.* A brown precipitate of osmium sulfide shows the presence of *Os*.

After cooling, add a few cc. of ether, shake the liquid, and remove the ether layer by means of a separatory funnel. Shake the solution repeatedly with ether until the ether extract appears colorless.

ETHEREAL SOLUTION. AQUEOUS SOLUTION (contains the remaining metals).

If the ethereal solution is yellow $AuCl_3$ is probably present.† *Evaporate off the ether, dissolve the residue in a little water, and test the resulting solution with $SnCl_2$.* The formation of a purple precipitate or color indicates the presence of *Au*.

Add ammonium acetate and formic acid and boil the solution for several hours, with the flask connected with a return-flow condenser. Filter and wash the precipitate with ammonium acetate and water.

PRECIPITATE (Pt, Pd, Ir, Rh, Ru, Hg). SOLUTION.

Heat the dried precipitate in a porcelain boat in a stream of hydrogen, which causes any Hg to be volatilized; it is subsequently condensed on the colder portions of the tube in the form of a gray coating. Boil the remaining metals, after becoming cold again, with hot HCl, in order to remove any Sn, or other foreign metal which may have been precipitated with this group on the addition of formic acid. Then mix the dry residue with common salt and heat to dull redness in a moist chlorine stream (the mass must not melt). After cooling treat the residue with water ‡ and add ammonium chloride to the solution as long as a precipitate is formed; filter.

PRECIPITATE [$(NH_4)_2PtCl_6$, $(NH_4)_2IrCl_6$, $(NH_4)_2RuCl_6$]. SOLUTION [Na_2PdCl_4, Na_3RhCl_6].

Dissolve the precipitate in hot water, add hydroxylamine hydrochloride, and allow the solution to cool. Again add NH_4Cl and filter.

Evaporate the solution slowly to dryness, with an excess of NH_4OH, and allow the residue to crystallize from a little warm, dilute NH_4OH (then filter off insoluble dark flocks; they usually consist chiefly of Ru). The Rh crystallizes as

Is rejected.

mation of "purple of Cassius", shows the presence of *Au*.	PRECIPITATE. $(NH_4)_2PtCl_6$.	SOLUTION. $[(NH_4)_3IrCl_6, (NH_4)_3RuCl_6.]$		chloropurpureo chloride in yellow crystals, which are filtered off. CRYSTALS: $Rh(NH_3)_5Cl_3$. MOTHER LIQUOR.		
	A yellow precipitate consisting of regular octahedrons shows the presence of *Pt*.	*Evaporate to dryness, ignite and fuse with KOH and KNO_3 in a silver crucible. Dissolve the melt in water and filter off the bluish-black residue.*		These are soluble in hot concentrated H_2SO_4, with a yellow color. *Mix a small portion with NaCl, heat in a stream of Cl, and dissolve the product in water.* A rose-colored solution, which is not precipitated by NH_4Cl when dilute shows the presence of *Rh*.	This contains palladiodiamine chloride. $Pd(NH_3)_4Cl_2$. *Saturate with conc. HCl, when crystalline $Pd(NH_3)_2Cl_2$ will be precipitated. Filter, dry in a stream of H, ignite and dissolve the residue in conc. HNO_3. Cautiously evaporate the brown solution to dryness, take up the residue in water and treat the solution with $Hg(CN)_2$.* A yellow precipitate shows the presence of *Pd*.
		RESIDUE. $(Ir(OH)_3)$.	SOLUTION. (K_2RuO_4).			
		Mix it with NaCl and heat in a current of chlorine. Dissolve the product in water and precipitate with NH_4Cl. A black precipitate shows the presence of *Ir*.	*Saturate in the cold with Cl, distill from a retort, and receive the vapors in alcohol that has been acidified with HCl.* A yellow-brownish precipitate shows the presence of *Ru*. It is confirmed by adding NH_4OH, a little $Na_2S_2O_3$, and warming. A deep violet coloration shows *Ru*.			

* MYLIUS and DIETZ, *Ber.*, 1896. 3187. They recommend this method for the *qualitative* examination only.
† Chromic acid will impart a yellow or blue color to the ether and $FeCl_3$ a yellow color.
‡ If a residue remains after extracting with water, it is filtered off and the process repeated; if this does not suffice, it is examined for Ir + Ru after fusing with KOH and KNO_3.

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INTERNATIONAL ATOMIC WEIGHTS, 1925

	Symbol	Atomic Weight		Symbol	Atomic Weight
Aluminium	Al	26.97	Mercury	Hg	200.61
Antimony	Sb	121.77	Molybdenum	Mo	96.0
Argon	A	39.91	Neodymium	Nd	144.27
Arsenic	As	74.96	Neon	Ne	20.2
Barium	Ba	137.37	Nickel	Ni	58.69
Beryllium	Be	9.02	Nitrogen	N	14.008
Bismuth	Bi	209.0	Osmium	Os	190.8
Boron	B	10.82	Oxygen	O	16.000
Bromine	Br	79.916	Palladium	Pd	106.7
Cadmium	Cd	112.41	Phosphorus	P	31.027
Calcium	Ca	40.07	Platinum	Pt	195.23
Carbon	C	12.000	Potassium	K	39.096
Cerium	Ce	140.25	Praseodymium	Pr	140.92
Cesium	Cs	132.81	Radium	Ra	225.95
Chlorine	Cl	35.457	Radon	Rn	222.
Chromium	Cr	52.01	Rhodium	Rh	102.91
Cobalt	Co	58.94	Rubidium	Rb	85.44
Columbium	Cb	93.1	Ruthenium	Ru	101.7
Copper	Cu	63.57	Samarium	Sa	150.43
Dysprosium	Dy	162.52	Scandium	Sc	45.10
Erbium	Er	167.7	Selenium	Se	79.2
Europium	Eu	152.0	Silicon	Si	28.06
Fluorine	F	19.00	Silver	Ag	107.880
Gadolinium	Gd	157.26	Sodium	Na	22.997
Gallium	Ga	69.72	Strontium	Sr	87.63
Germanium	Ge	72.60	Sulfur	S	32.064
Glucinum	Gl	9.02	Tantalum	Ta	181.5
Gold	Au	197.2	Tellurium	Te	127.5
Helium	He	4.00	Terbium	Tb	159.2
Holmium	Ho	163.4	Thallium	Tl	204.39
Hydrogen	H	1.008	Thorium	Th	232.15
Indium	In	114.8	Thulium	Tm	169.4
Iodine	I	126.932	Tin	Sn	118.70
Iridium	Ir	193.1	Titanium	Ti	48.1
Iron	Fe	55.84	Tungsten	W	184.0
Krypton	Kr	82.9	Uranium	U	238.17
Lanthanum	La	138.90	Vanadium	V	50.96
Lead	Pb	207.20	Xenon	Xe	130.2
Lithium	Li	6.940	Ytterbium	Yb	173.6
Lutecium	Lu	175.0	Yttrium	Yt	88.9
Magnesium	Mg	24.32	Zinc	Zn	65.38
Manganese	Mn	54.93	Zirconium	Zr	91.